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N. C. Davis
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May 1992

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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PREFACE

This report was originally published in April 1982 and is being reissued at this time.

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Richland, Washington 99352

SUMMARY

Pacific Northwest Laboratory (PNL) has evaluated, on a laboratory scale, the characteristics and pellet fabrication properties of UO_3 powder prepared by the thermal denitration process. Excellent quality, 96% TD (percent of theoretical density) pellets were produced from developmental lots of this powder. Apparently, the key to making this highly sinterable powder from uranyl nitrate is the addition of ammonium nitrate (NH_4NO_3) to the feed solution prior to thermal denitration. The developmental lots of UO_3 powder were supplied by Oak Ridge National Laboratory (ORNL). These powder lots were processed with and without the NH_4NO_3 addition in the feed solution. The lots included samples from the ORNL laboratory rotary kiln and from a larger scale rotary kiln at National Lead of Ohio (NLO).

In the PNL evaluation, samples of the UO_3 were calcined and reduced to UO_2, followed by conventional process procedures to compare the sinterability of the powder lots. The high density pellets made from the powder lots, which included the NH_4NO_3 addition, were reduced to Fast Breeder Reactor (FBR) density range of 88 to 92% TD by the use of poreformers.

The NH_4NO_3 addition also improved the sinterability properties of uranium oxide powders that contain thorium and cerium. Thorium and cerium were used as "stand-in" for plutonium used in urania-plutonia FBR fuel pellets. A very preliminary examination of a single lot of thermally denitrated uranium-plutonium oxide powder was made. This powder lot was made with the NH_4NO_3 addition and produced pellets just above the FBR density range.

The experience and information gained from this UO_2 and mixed-oxide work will be used to develop the uranium-plutonium oxide fuel pellet process for FBR fuel when larger quantities of the mixed-oxide powders become available.

CONTENTS

FIGURES

FIGURES (Contd)

TABLES

INTRODUCTION

Large-scale commercial operations have produced uranium dioxide (UO_2) powders by denitration of uranyl nitrate followed by hydrogen reduction[1]. However, the properties of these oxide powders are not normally amenable to the fabrication of UO_2 pellets. Excessive milling or other comminution methods are required to activate the powder for satisfactory sintering. A thermal denitration method for co-conversion of uranyl nitrate-plutonium nitrate solutions is being developed at Oak Ridge National Laboratory (ORNL)[2].

As a participant in the conversion-fabrication program, Pacific Northwest Laboratory (PNL) evaluated pellet fabrication properties of powder produced by the thermal denitration process. This program is sponsored by the Department of Energy (DOE) and is shared by three laboratories: 1) ORNL is developing the thermal denitration process to produce UO_3; 2) PNL, as detailed in this report, has demonstrated the feasibility of processing and fabricating pellets with Fast Breeder Reactor (FBR) densities of 88 to 92% TD from the ORNL powder lots; and 3) the Hanford Engineering Development Laboratory (HEDL) will scale the process up to production levels. The program is managed by the HEDL Technology Management Center for Reactor Fuels and Materials.

This report describes a laboratory batch process for fabrication of pellets from thermally denitrated powder. In screening tests the procedures were kept constant to evaluate and compare each of the powder lots. In other tests, pellet densities were reduced to the FBR density specification by the use of poreformers. In addition, a limited evaluation of a modified batch denitration from ORNL indicated FBR densities could be obtained by control of the thermal denitration process parameters. The experience and information gained from these development tests may be transferred to develop a mixed-oxide process when sufficient quantities of powders become available.

CONCLUSIONS AND RECOMMENDATIONS

The results of the PNL laboratory studies indicate the following conclusions and recommendations for additional evaluation.

- The presence of NH_4NO_3 in the thermal denitration feed solution greatly improved sintering properties of the oxide.
- In powder lots converted with the NH_4NO_3, high quality test pellets were fabricated to densities greater than 96% TD using conventional processes without any powder milling. The thermal denitration process parameters, which included a wide range of temperatures, feed rates and concentrations, had little effect on pellet fabrication or final density.
- Powder process parameters and properties that yielded high densities included calcine temperatures from 600 to 800°C, surface areas of 4 to 10 m^2/g, tap density about 1 g/cm^3, and oxygen to metal (O/M) ratio of 2.1 to 2.2.
- Conversely, lots processed without the NH_4NO_3 in the denitration feed solution produced powders with dense, large granules that were not amenable to pellet fabrication. Excessive milling improved the sintering properties of the powder; however, milling still did not yield powder properties comparable to powder produced with the NH_4NO_3 addition.
- FBR densities, 88 to 92% TD, were achieved from the highly sinterable thermal denitrated powder by use of ammonium oxalate poreformers. These densities were duplicated to a limited extent using UO_3 granules as a poreformer.
- Powders produced in a modified batch denitration process, as opposed to the powder lots from the ORNL rotary kiln, had lower surface area ($\sim$3 m^2/g), fewer submicron particles and could be conventionally processed without poreformers to the FBR density range.
- A single lot of U-Pu thermally denitrated powder (processed with the NH_4NO_3 addition) produced pellets just above the FBR range using

the fabrication conditions developed from work with the UO_2 powder lots.

This study also indicated that additional development and evaluation is needed in several areas. Additional thermal denitration runs should be made to develop an improved powder morphology for pellet fabrication. The small batch denitration test evaluated during this study indicated that powder properties affecting sinterability could be controlled during the conversion. The development and evaluation of this type of powder should be continued. The target goal for this development would be to: 1) change powder morphology to increase tap density by reducing submicron particles, which would reduce the pressure required to press pellets and eliminate the top punch holddown required during pellet ejection, and 2) control the sinterability of the powder by denitration process conditions.

Other recommendations for future work include:

- controlling lot-to-lot consistency in large continuous rotary operations
- developing and evaluating a continuous furnace for calcine reduction operations
- developing U-Pu mixed-oxide thermal denitration and pellet fabrication process
- fabricating and evaluating an irradiation test made up of pellets produced from thermally denitrated powder.

PROCESS DESCRIPTION

The process used for the laboratory evaluation of the thermally denitrated UO_3 powder lots is shown in Figure 1. The following discussion of the process highlights the evaluation details. In the initial screening tests, procedures were kept constant to evaluate UO_3 powder preparation conditions. Process variations were introduced in other tests to alter powder characteristics and evaluate those changes on the sinterability of the pellets.

UO_3 POWDER PREPARATION

The powder lots evaluated in this study were produced by thermal denitration of uranyl nitrate. These UO_3 powder lots were produced at ORNL during development of the conversion process. The process flow chart (Figure 1), includes the UO_3 preparation step to link the ORNL preparation conditions[2] with subsequent evaluation steps. The UO_3 powder lots were received, weighed and assigned a PNL identification number. The Th-D numbers used throughout these studies are referenced to the ORNL identification in Tables 1, 2 and 3. The as-received UO_3 bulk density[a] and surface area[b] were determined before calcining and reducing.

CALCINATION/REDUCTION

The as-received UO_3 powder was calcined in a batch furnace to remove moisture and residual volatile material and to reduce the UO_3 to UO_2. This calcination reduction process should not be considered a reference process because a continuous calcine furnace would be preferred over the batch-type laboratory process used in this study. The furnace was a cold-wall, refractory metal resistance heated furnace, normally used for high temperature sintering.

During a standard screening cycle, as many as five 100 g samples were processed in stainless steel trays. The furnace was evacuated to approxi-

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[a] ASTM Standard B-212-48.

[b] BET gas adsorption method.

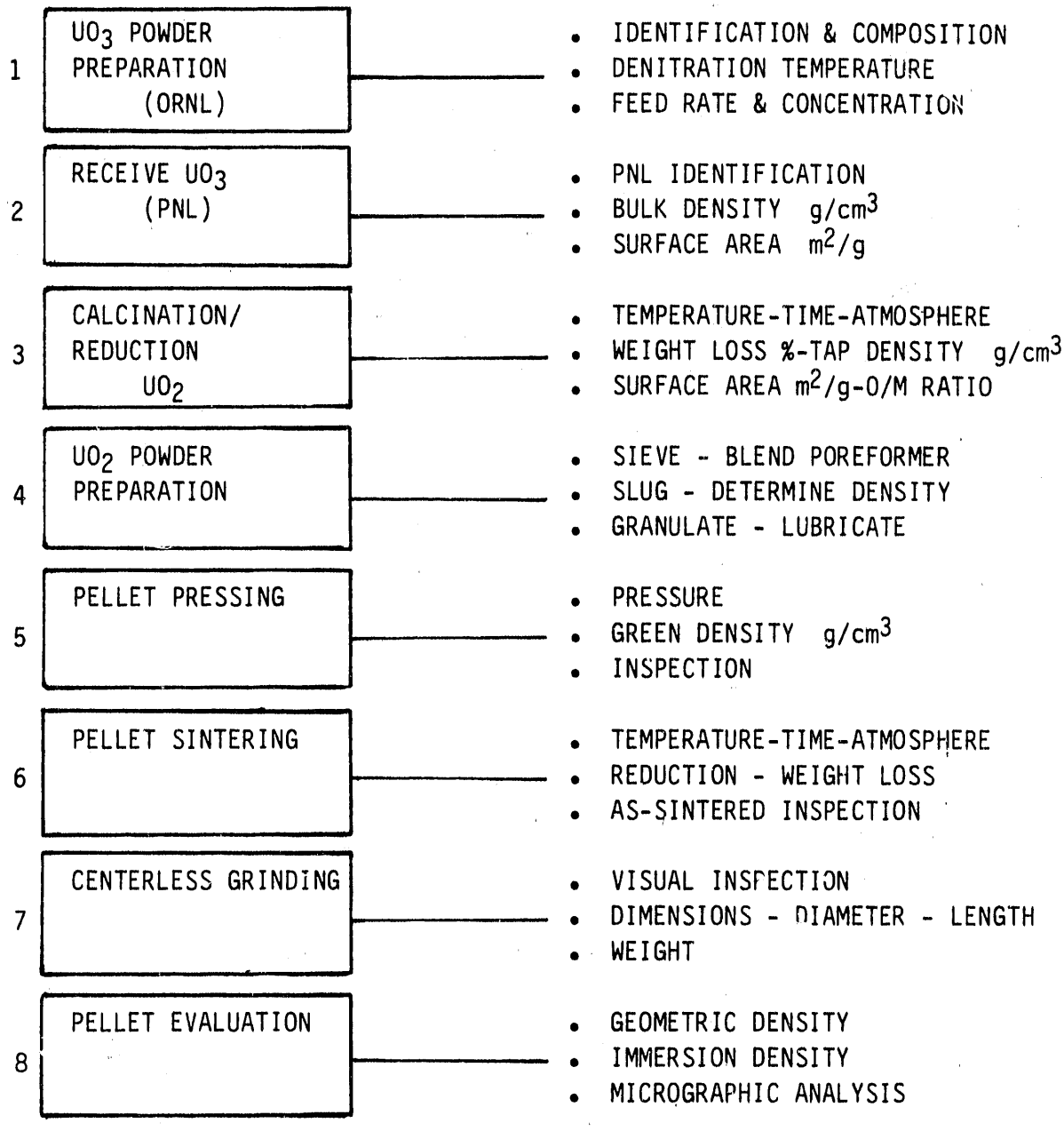

FIGURE 1. Process Flow Chart with Evaluation Procedure.

mately 30 in. vacuum and back-filled with argon. The furnace was heated at a rate of 300°/h with argon flowing over the trays of powder. At 600°C, hydrogen was introduced to complete the reduction of UO_3 to UO_2. The furnace temperature was held at 600°C for 4 h with a 50% argon/50% hydrogen atmosphere. Again, this method should not be considered a reference process for production use. By using a continuous calciner and allowing the argon-hydrogen mixture to pass directly through a powder bed, less H_2 would be required to effect the desired reduction. After 4 h at temperature, the reduced UO_2 was cooled 300°C/h in argon. To reduce the possibility of powder oxidation when the furnace was opened to air, the furnace remained closed in a static argon atmosphere overnight. After the calcination/reduction cycle, the weight loss, tap density, O/M and surface area were measured. In addition to the standard screening tests, the calcination/reduction temperature was varied to determine its effect on the powder fabrication properties.

UO_2 POWDER PREPARATION

After calcination and reduction, the UO_2 powder, denitrated with the NH_4NO_3 addition, consisted of fine, fluffy particles with relatively low tap density. Pressure as high as 25 kpsi was needed in the slugging (pre-pressing) operation to obtain conventional slug densities of about 4.3 g/cm^3. These slugs (~50 g, 0.2 in. thick from a 2-in. die) were granulated to pass through a 20 mesh screen. Approximately 80% of the granulated powder remained between 20 and 100 mesh screens. In the standard screening tests, 0.3 wt% zinc stearate was blended with the granulated UO_2 to provide lubrication for pellet pressing.

In some tests, poreformers were used to reduce pellet density. Poreformers in a selected particle size range were blended with the -100 mesh UO_2 before the powder was slugged. The standard screening-test procedure was then continued.

PRESSING

Pellets were pressed using an automatic, double action hydraulic press. This 12-ton press can be operated fully automatically, semi-automatically,

or manually. The semi-automatic mode was used to evaluate the relatively small quantities of powder. The die was filled manually with the desired quantity of powder. Then in the semi-automatic mode, the powder was lowered in the die (i.e., the pellets were pressed in an underfill mode). Pressure was applied by the upper and lower punches, and the pellet was ejected and removed from the die by hand. Other hydraulic features used in pressing the pellets included deceleration of the punches, prepress and press dwells, and top punch hold-down during ejection. The top punch hold-down provided slight pressure restraint on the pellet during ejection to prevent capping or defects to the end of the pellet. With this feature, higher pressures could be used without causing defects in the green pellets.

Pressures of 40 to 50 kpsi were used in these screening tests to press 8 to 10 pellets from each powder lot. The pellets were 0.425 in. in diameter and were pressed to provide a length to diameter ratio of about 1:1. Some tests were made using a 0.25 in. diameter die to determine the effect that pellets sized to FBR specifications would have on pellet fabrication. Conditions were kept constant for direct comparison of the different powder lots.

The green pellets were identified, measured, weighed, visually inspected, and density was calculated. In addition, the green pellets were spot checked for physical integrity by submerging them in alcohol. In cases where defects such as cracks or end-caps were present but not visible, bubbles would stream from the defect.

PELLET SINTERING

Test pellets were placed in molybdenum sintering boats and sintered in a cold-wall all metal, batch-type furnace similar to the one used in the calcination/reduction cycle. In the screening tests, the furnace was programmed to heat 150°C/h to 450°C, 300°C/h to 1700°C, held at 1700°C for 8 h, and cooled at a rate of 400°C/h. The atmosphere was 50% hydrogen/ 50% argon flowing at a rate of 20 cfh for the entire cycle.

In subsequent tests, the time was reduced to 4 h for comparison to the 8-h runs. Resinter tests were run for 24 h at 1700°C. The heating rate was reduced to 50°C/h between 300 and 400°C in tests that included poreformers.

PELLET GRINDING

The test pellets were ground with a centerless grinder equipped with diamond wheels. This grinder provided a uniform finish for inspection and accurate dimensional measurements.

PELLET EVALUATION

Pellet evaluation, the final step in the process flow, included geometric and immersion density determinations, visual inspection and microstructural examination. Typical micrographs of test pellets are shown throughout this report. Densities shown in this report were determined by water immersion[a] unless otherwise noted. The percent of theoretical density for UO_2 is based on 10.96 g/cm^3.

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[a] ASTM Standard B-212-48.

PROCESS DISCUSSION

This section discusses the as-received data furnished by ORNL and compares the UO_3 properties of the various powder lots. Discussion of pellet fabrication by the standard screen test is included. Observations made during these tests lead to additional process evaluation discussed in the latter part of this section.

UO_3 POWDER PREPARATION

Thermally denitrated UO_3 powder lots evaluated in this study were processed at ORNL and NLO. The various process conditions, as furnished by ORNL, and the as-received powder properties, measured at PNL, are shown in Tables 1, 2 and 3.

The UO_3 powder lots were processed with NH_4NO_3 in the feed solution over a wide range of denitration conditions (Table 1). In reviewing these conditions, neither the range of denitration temperatures, nor the variations in feed concentrations or product rate had much influence on the physical properties of the powder. However, the powder properties were affected by the presence of NH_4NO_3 in the feed solution. In contrast to the lot processed without NH_4NO_3, the powder lots processed with NH_4NO_3 produced oxide with high surface areas (small particles) and low bulk densities. During denitration, the NH_4NO_3 addition results in the formation of the double salt (ammonium nitrate-uranyl nitrate), which has beneficial effects on the physical properties of the oxide.(2)

Powder lot Th-D-3 (Table 1) was prepared without NH_4NO_3 and the physical properties were not amenable to sintering. The powder lot had lower surface area and higher bulk density than powders with the NH_4NO_3 addition. Apparently, the NH_4NO_3 promotes the formation of very soft agglomerates of fine particles instead of the hard, dense granules normally produced in the conversion of uranyl nitrate.

Demonstration runs in larger rotary kiln at National Lead of Ohio (NLO) (Table 2) expanded the processing conditions to product rates of 3 kg/h,

TABLE 1. Denitration Conditions and As-Received Properties of ORNL UO_3 Powder Lots Produced in 8 cm ID x 80 cm Rotary Kiln. All Powder Lots with NH_4 +/U Feed Mole Ratio of 2.0 Unless Otherwise Noted.

ORNL Rot No.	Tube Temp., °C	Product Rate, g UO_3/h	Feed Conc., UM	Powder Properties of As Received UO_3		
				PNL Th-D No.	Surface Area, m^2/g	Bulk Density, g/cm^3
14P(a)	500	NA	1.4	3	0.89	2.50
32P(b)	430	NA	1.7	4	6.86	1.04
34	430	0.36	1.7	5	8.61	0.97
35	500	0.36	1.7	6	11.52	0.95
37	390	0.36	1.7	7	8.83	0.96
55	525	0.50	2.0	17	11.15	0.83
49	495	0.36	1.7	18	8.12	0.95
41	620	0.36	1.7	19	9.71	0.95
56A	475	0.80	2.0	20	11.47	0.77
56C	525	0.76	2.0	21	10.94	0.72
57	420	0.38	1.7	22	10.47	0.78
58	455	0.42	2.0	23	10.06	0.87
59	455	0.42	1.7	24	11.37	0.77
60	450	0.42	2.3	25	9.38	0.84

(a)Prepared without NH_4NO_3 addition.

(b)Feed NH_4 +/U Ratio of 1.3 M/M.

TABLE 2. Denitration Conditions and As-Received Properties of UO_3 Powder Lots, Produced in NLO[a] 16 cm x 65 cm Rotary Kiln. Production Rate 3 kg/h.

Test No.	Tube Temp., °C	Feed Solution NH_4^+/U Mole/Mole	Feed Solution NO_3^-/U[b] Mole/Mole	Surface Area, m^2/g	Bulk Density, g/cm^3	PNL Th-D No.
A-1	605	2.0	2.0	7.23	0.82	12
A-2	405	2.1	1.9	6.30	0.70	13
B-1	750	0	3.9	0.92	1.79	14
B-2	605	0	4.0	1.46	1.78	15
B-3	445	0	3.9	0.70	1.93	16

(a) National Lead of Ohio.

(b) NO_3 present as NH_4NO_3 not included: solutions with ratios <2 are acid deficient; solution >2 have excess NO_3.

TABLE 3. Denitration Conditions and As-Received Properties of ORNL Thorium Oxide and Uranium Oxide Powder Lots containing Th and Ce Produced in NLO Rotary Kiln.

ORNL Rot No.	Composition	U / U+Th+Ce, Mole %	NH_4^+ / U+Th+Ce, Mole %	Tube Temp., °C	Surface Area, m^2/g	Bulk Density, g/cm^3	PNL Th-D No.
44	$UO_3 + ThO_2$	75	2.0	500	15.6	0.50	8
53	$UO_3 + ThO_2$	25	1.0	540	17.9	0.70	9
51	THO_2	0	5.0	550	25.8	0.75	10
43	$UO_3 + Ce_2O_3$	75	2.0	460	6.0	0.65	11

both with and without the NH_4NO_3 addition. The as-received powder properties of the NLO powder are similar to the ORNL runs.

Powder preparations by ORNL also included powder lots containing thorium and cerium. The U-Th and U-Ce oxide powder lots (Table 3) were evaluated to provide an indication of mixed oxide (U-Pu) sintering behavior. The high surface area and low bulk density was attributed to the NH_4NO_3 used in the denitration feed solution.

FABRICATION SCREENING TESTS

Samples of each thermally denitrated powder lot (Tables 1, 2 and 3) were evaluated in fabrication screening tests. The process procedure, shown in Figure 1, was followed to determine and compare the sinterability of each powder lot. Fabrication data from the screening tests are summarized in Tables 4, 5 and 6.

Powder lots from the ORNL rotary kiln, which included NH_4NO_3 in the denitration feed (Table 4), all sintered to greater than 96% TD. These high density pellets were obtained from a wide range of powder properties and processing parameters (Table 1 and 4). In all these powder lots, the NH_4NO_3 feed addition was a common requirement for high density pellets. Pellets fabricated from these powder lots were relatively crack-free and had a uniform high-density structure. Typical microstructures are shown in Figures 2 and 3. The pellet shown in Figure 2 was made from a mixture of four of the earlier lots (Th-D-4 through -7) and Figure 3 is one of the last powder lots (Th-D-25) evaluated.

Powder lot Th-D-3, prepared without the NH_4NO_3 addition, consisted of hard, glossy granules with a surface area of less than 1 m^2/g after calcining and reducing. When pressed and sintered, the pellets were poor quality and less than 70% dense. After the powder was vibratory milled for 2, 3, and 5 h, some small, hard granules still remained, and the pellets were pressed and sintered to 89.7, 93.6 and 94.6% TD, respectively. The quality of these pellets was marginal. A typical pellet microstructure is shown in Figure 4.

TABLE 4. UO_2 Screening Test Summary, Including Powder and Pellet Data for the ORNL Powder Lots.

PNL Th-D No.	Cal./Red. wt loss, %	UO_2 O/M, Ratio	Surface Area, m^2/g	Density, g/cm^3			Sintered % TD
				Tap	Slug	Green	
3(a)	6.6	NA	3.18	NA	5.0	6.52	89.70
4	16.2	2.26	9.60	1.23	3.77	5.09	97.40
5	11.7	2.24	7.17	1.21	4.12	5.29	97.80
6	8.1	2.23	8.07	1.26	4.24	5.27	98.10
7	12.1	2.25	7.33	1.24	4.30	5.23	98.10
17	7.1	2.18	10.61	0.97	4.30	5.17	97.65
18	9.7	2.13	6.91	1.08	4.38	5.38	97.70
19	5.5	2.15	8.89	1.20	4.53	5.38	97.44
20	8.5	2.17	9.85	0.84	4.21	5.03	97.37
21	6.9	2.21	11.91	0.86	4.18	5.00	97.38
22	11.2	2.17	10.33	0.87	4.21	5.06	97.74
23	9.3	2.13	9.54	1.00	4.20	5.10	97.35
24	8.0	2.13	8.62	0.96	4.22	5.10	97.20
25	10.0	2.13	8.98	1.04	4.33	5.14	97.40

(a)Fabrication data after UO_2 Powder was vibratory milled 2 h.

TABLE 5. UO_2 Screening Test Summary, Including Powder and Pellet Data for the NLO Denitration Powder Lots.

PNL Th-D No.	Cal./Red. wt loss, %	UO_2 O/M Ratio	Surface Area, m^2/g	Density, g/cm^3			Sintered, % TD
				Tap	Slug	Green	
12	3.9	2.11	6.49	1.15	4.18	5.12	97.2
13	9.0	2.12	6.46	1.08	4.12	4.03	97.6
14	3.7	2.10	57	3.28	5.21	6.0	79.9
15	6.0	2.11	3.91	3.53	5.31	6.15	81.8
16	7.0	2.08	2.51	3.55	4.68	6.25	79.7

1) Powder lots 12 and 13 were similar to ORNL lots prepared with NH_4NO_3.
2) Powder lots 14, 15 and 16 were processed without NH_4NO_3.
3) A composite of powder lots 14, 15 and 16 was vibratory milled for 4 h, increasing the surface area to 4.52 m^2/g, and sintered to 93.7% TD with good quality pellets.

TABLE 6. Mixed Oxide Screening Test Summary, Including Powder and Pellet Data for the ORNL Powder Lots Processed with Thorium or Cerium Additions.

PNL Th-D No.	Oxide Comp. Mole %	Cal./Red. wt loss, %	Surface Area, m^2/g	Density, g/cm^3			Sintered, % TD
				Tap	Slug	Green	
8	75U-25Th	5.6	13.31	0.96	4.22	5.00	97.3
9	25U-75Th	3.9	23.00	1.06	4.33	4.04	93.4
10	100Th	1.1	32.15	1.13	4.90	5.40	91.9(a)
11	75U-25	8.7	6.86	1.21	4.25	5.07	92.7(a)

(a) Quality of pellets from Powder lots 10 and 11 was poor. The rejects were due to small cracks.

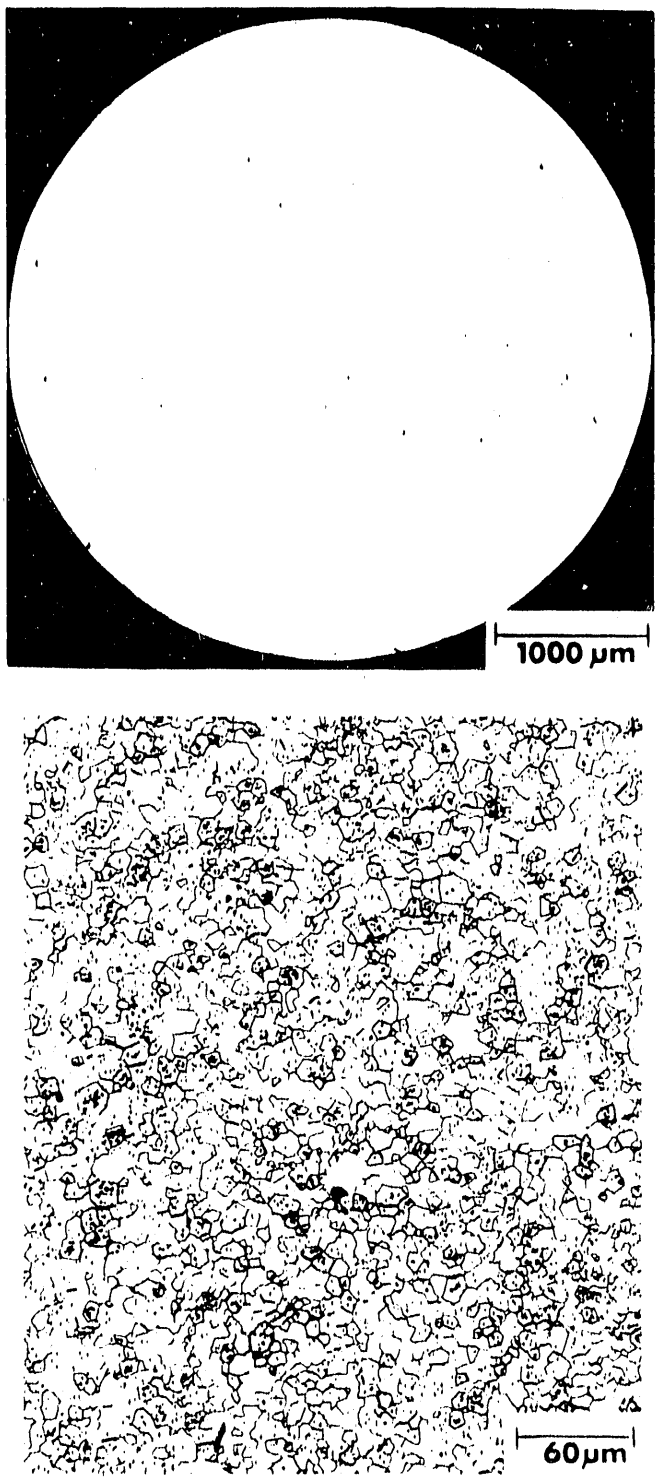


FIGURE 2. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-4 through -7 (Composite), 97.8% TD.

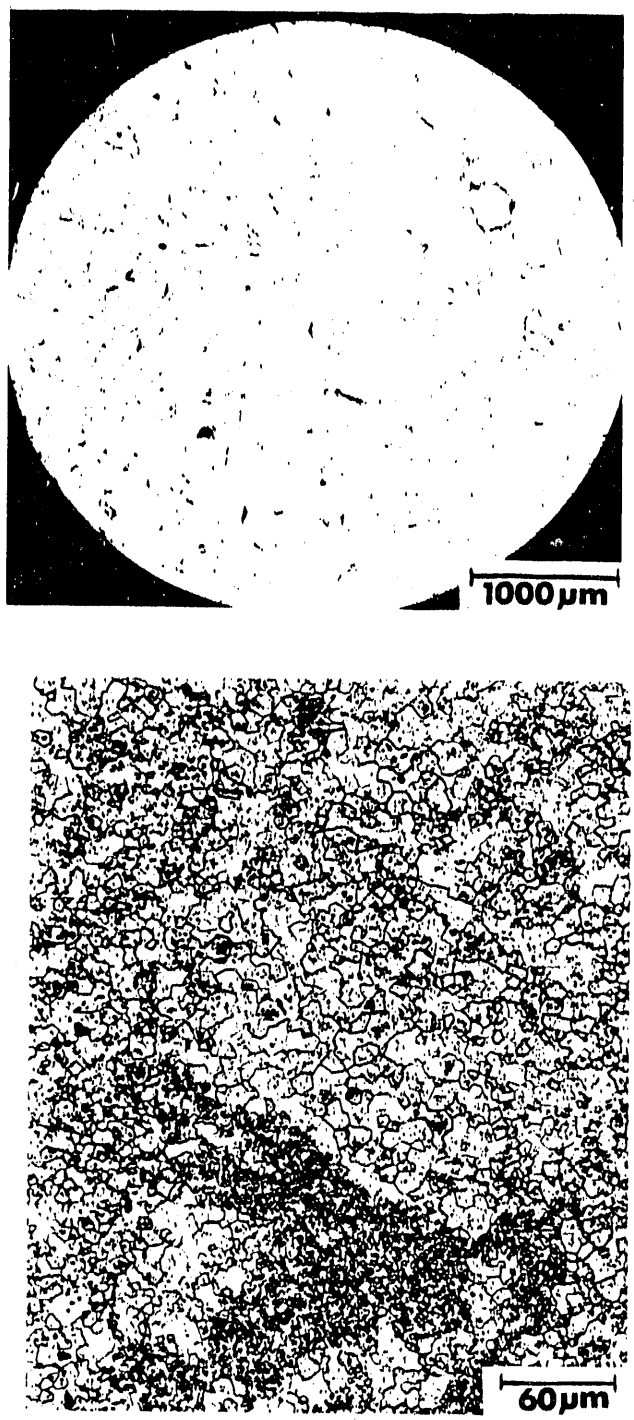


FIGURE 3. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-25, 96.9% TD.

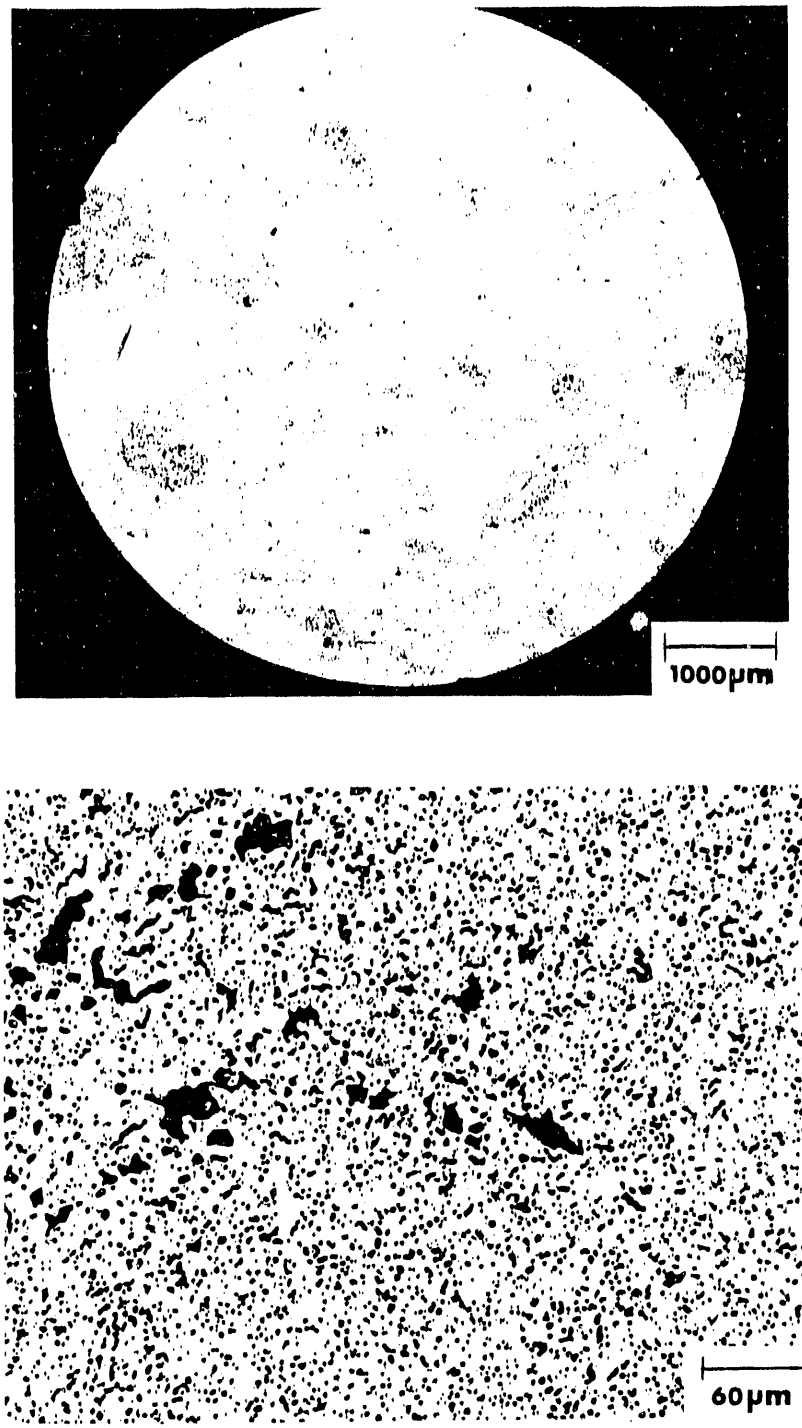


FIGURE 4. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-3 (ORNL Powder Lot Without NH_4NO_3 Addition), Vibratory Milled 2 h, 89.7% TD.

Results of screening tests for the scale-up batches of the powder processed at NLO were similar to screening test results attained for lots produced at ORNL. The pellet fabrication data are given in Table 5. Powder lots Th-D-12 and 13, which contained the NH_4NO_3 addition, produced 96% to 97% TD pellets. The powder lots Th-D-14, -15 and -16, which did not have the NH_4NO_3 addition, sintered to 79 to 80% TD. However, vibratory milling for 1 h increased the pellet density to 86% TD, and after 4 h of milling pellet density increased to 93.7% TD (Figure 5). All of the low density pellets made from the NLO powder lots without the NH_4NO_3 addition were sound, high quality pellets as opposed to the poor quality pellets from the ORNL powder lot Th-D-3, processed without the NH_4NO_3 addition.

Pellet fabrication data for UO_2 powders containing thoria and ceria are shown in Table 6. The same screening process was used to enable a comparison to the existing UO_2 data base. These mixed oxide powder lots had high surface areas and low bulk densities (Table 3). They were more difficult to process than the UO_3 powder lots. Lower sintered densities were achieved, and some defects were observed. The microstructure of these mixed oxide pellets is illustrated in Figures 6 through Figure 9.

A single lot of 24 mole% Pu-76 mole% U powder was prepared by thermal denitration at 550°C using the same method developed for uranium oxide. The feed solution contained the NH_4NO_3 addition to improve the fabrication properties of the powder. The as-received bulk density and surface area were 0.45 g/cm^3 and 9.2 m^2/g respectively. This powder lot was calcined, pressed, and sintered into pellets following the process and conditions outlined for the standard screening test.

The tap density after calcining was 1.22 g/cm^3 while the surface area was 10.2 m^2/g. After slugging and granulating, the calcined powder was pressed into pellets with an average green density of 5.39 g/cm^3. These pellets sintered to 93.9% TD. The density of these U-Pu oxide pellets was lower than the UO_2 pellets, but about the same as the U-Th and U-Ce oxide pellets.

Tables 4, 5 and 6 show that the addition of NH_4NO_3 to the feed solution produced an active sinterable powder, whereas powders prepared without

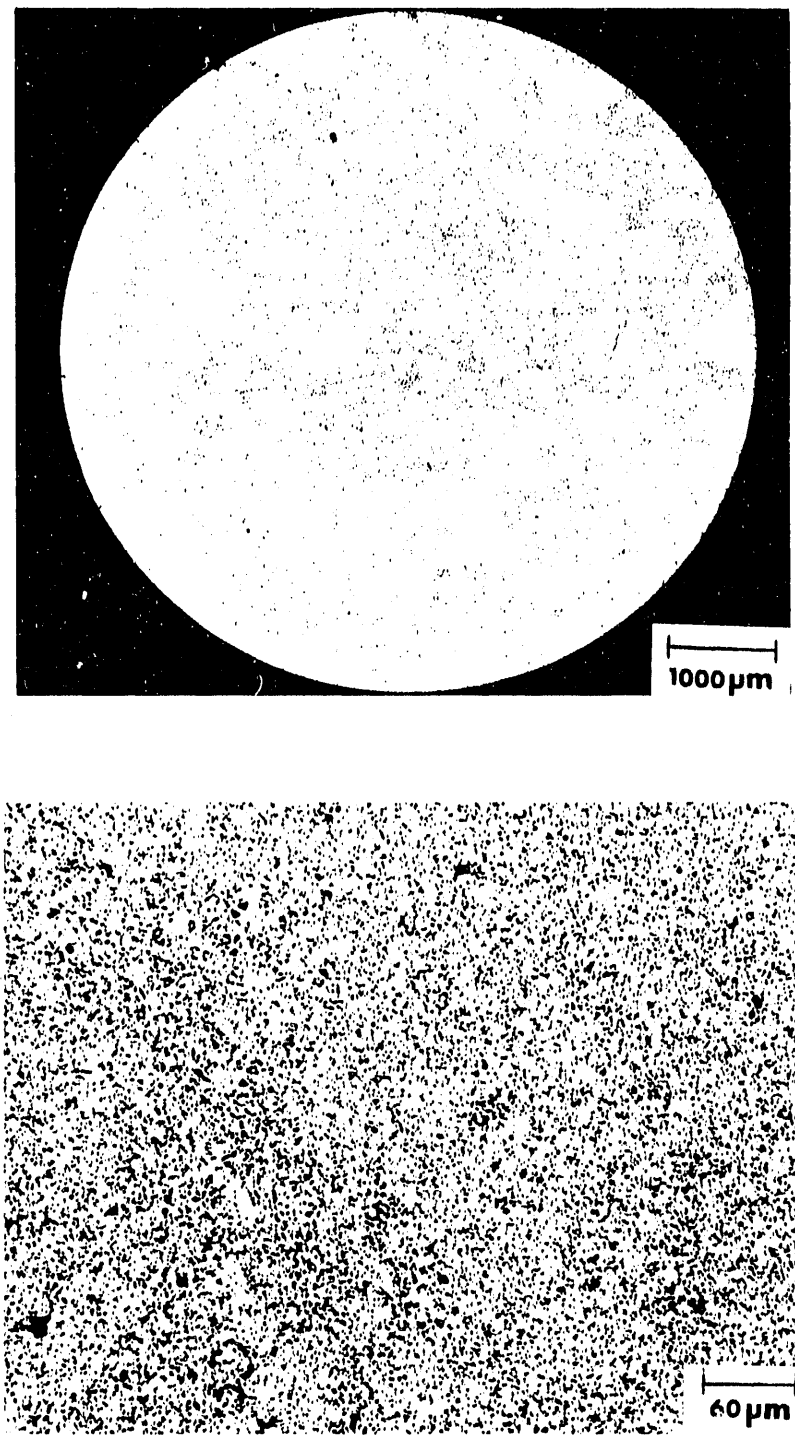


FIGURE 5. Microstructure of UO_2 Pellet Made from Powder Lots Th-D-14, 15, and 16 (Composite); NLO Powder Without NH_4NO_3 Addition, Vibratory Milled 4 h, 93.7% TD.

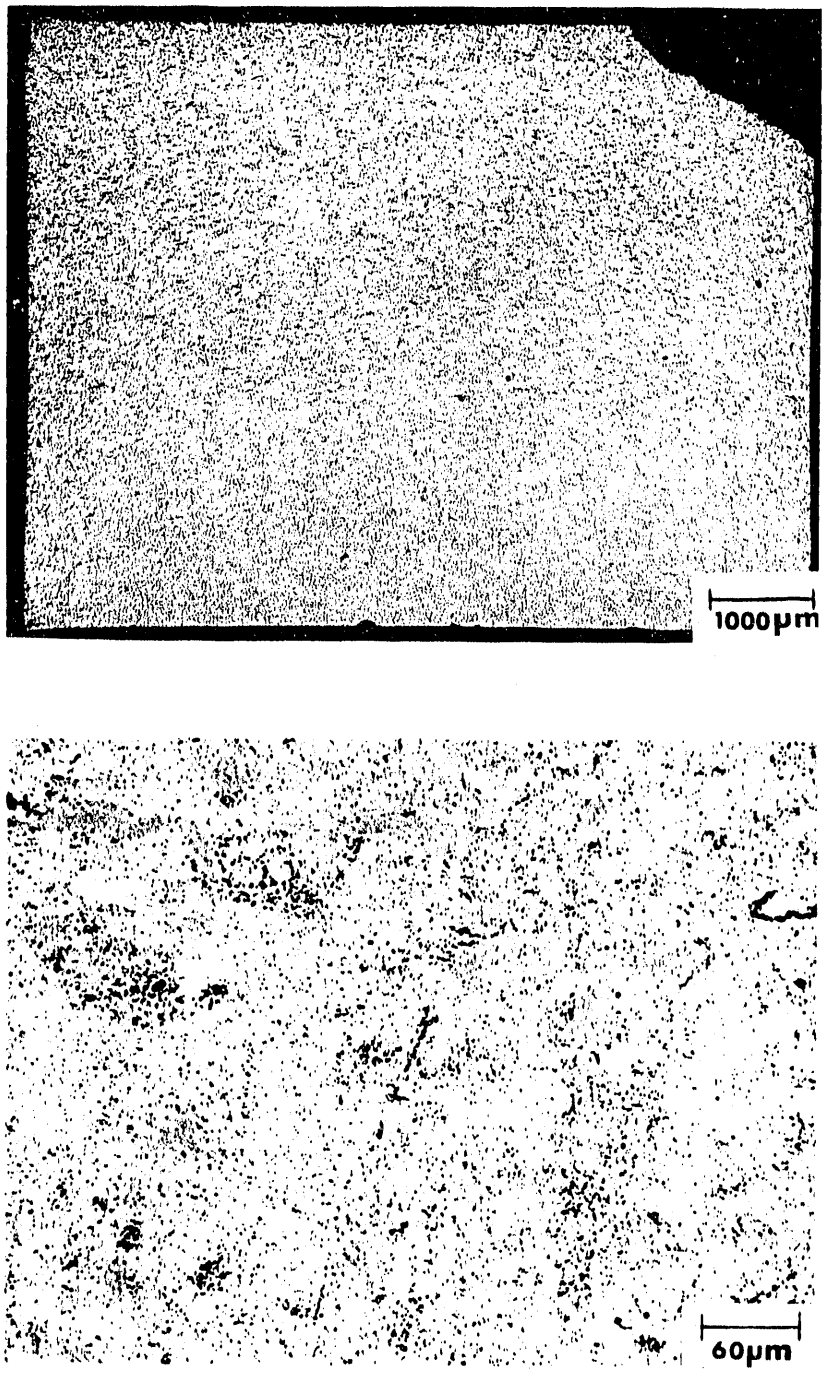


FIGURE 6. Microstructure of Mixed Oxide Pellet Made from Powder Lot Th-D-8 $(U_{0.75},Th_{0.25})O_2$, 97.3% TD.

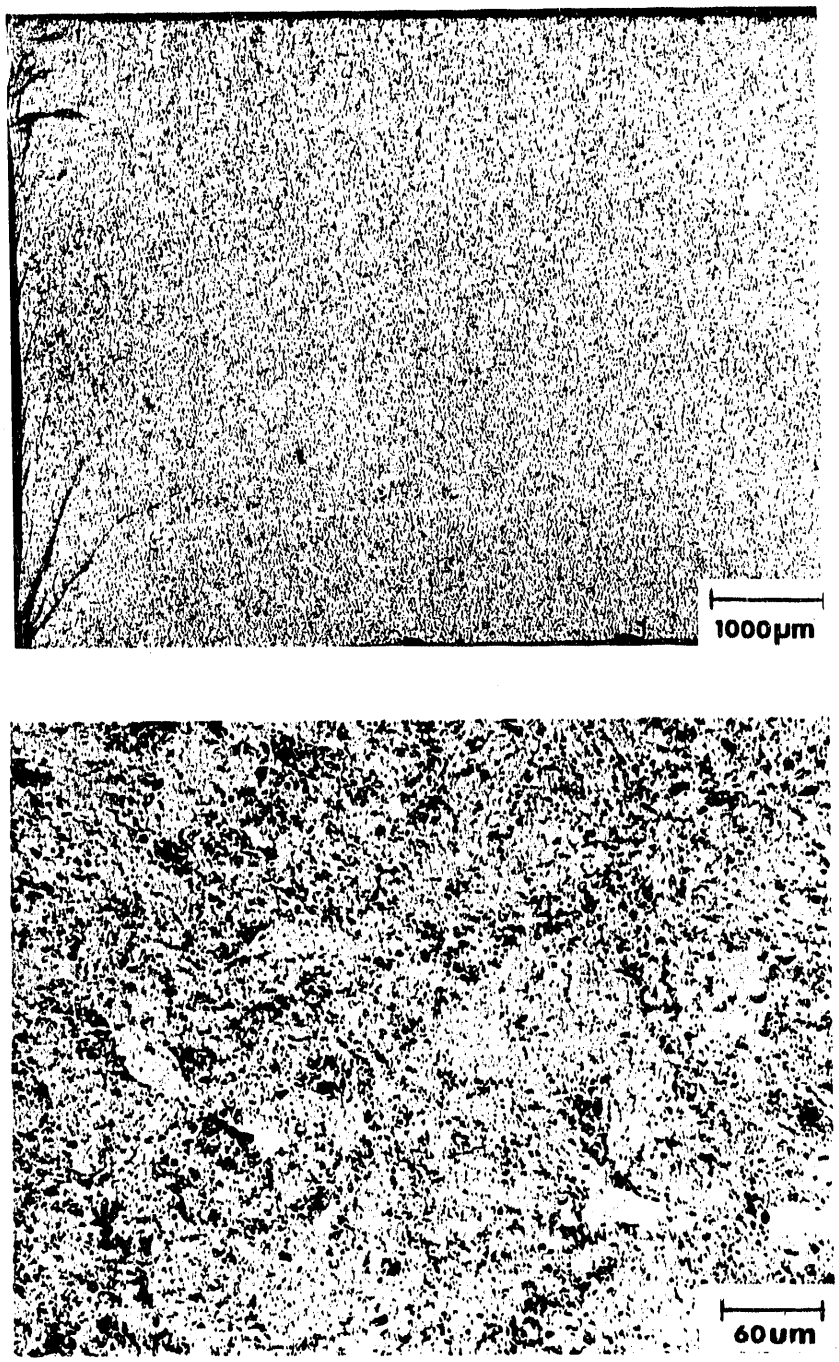


FIGURE 7. Microstructure of Mixed Oxide Pellet Made from Powder Lot Th-D-9 $(U_{0.25},Th_{0.75})O_2$, 93.4% TD.

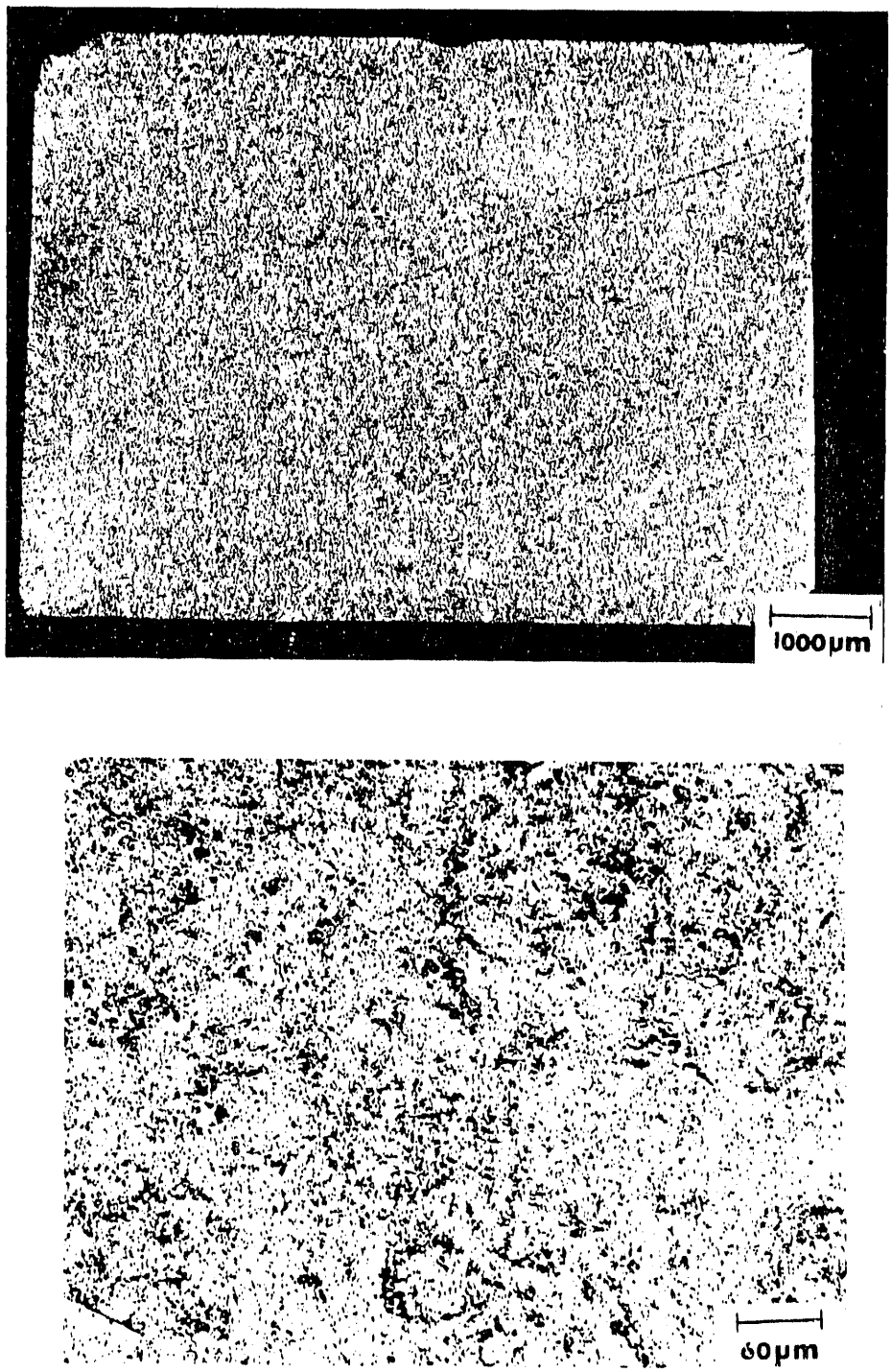


FIGURE 8. Microstructure of ThO_2 Pellet Made from Powder Lot Th-D-10, 91.9% TD.

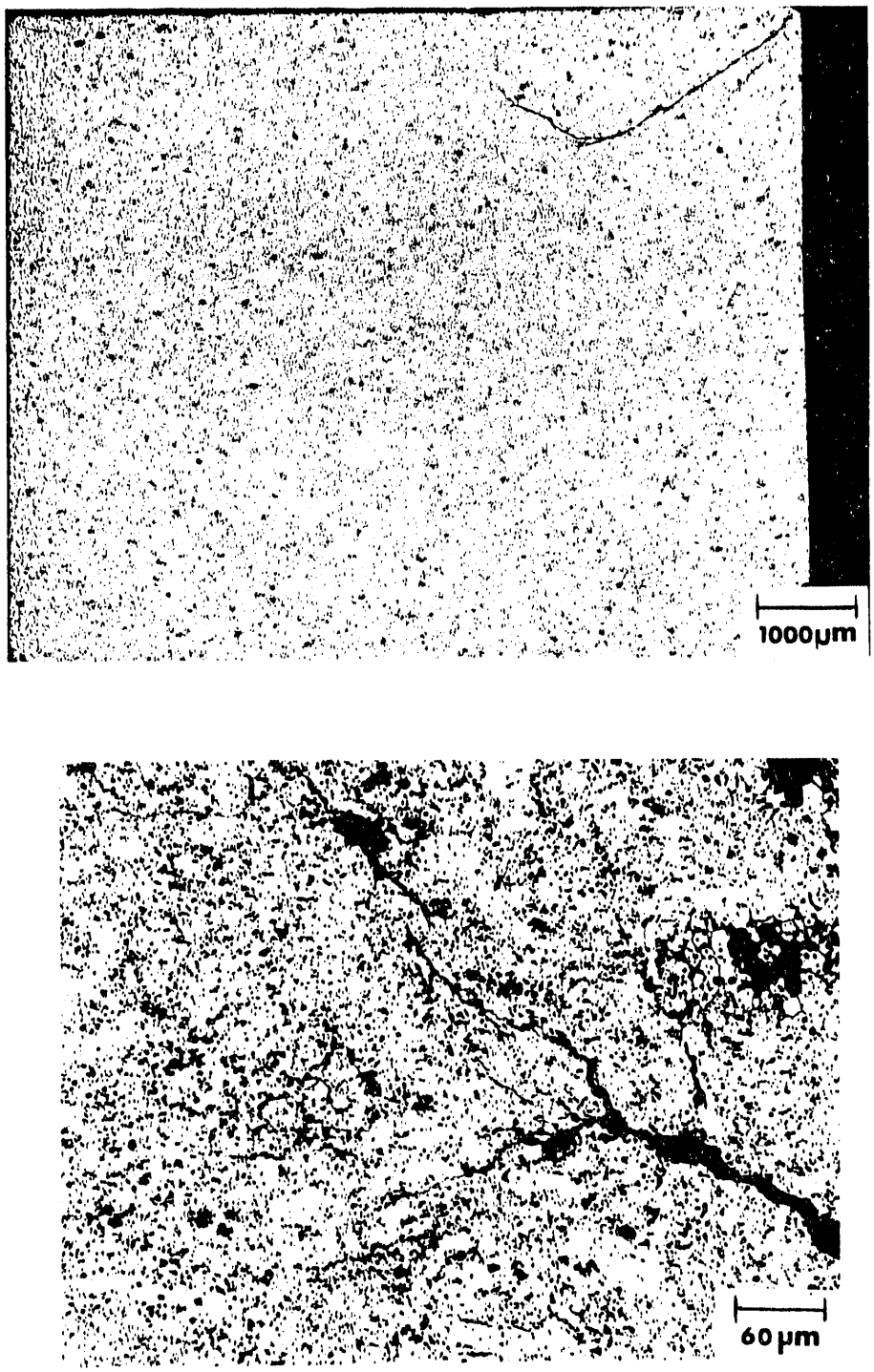


FIGURE 9. Microstructure of Mixed Oxide Pellet Made from Powder Lot Th-D-11 $(U_{0.75},Ce_{0.25})O_2$, 92.7% TD.

NH_4NO_3 addition sintered to lower densities and required excessive milling to increase the powder activity and pellet density.

PROCESS OBERVATIONS

The processing and evaluation of the first powder lots, Th-D-4 through -7 produced good quality green pellets. These test pellets were relatively free of defects and sintered to densities greater than 97% TD (Table 4). The conventional and simple three-step pressing operation (fill, press, and eject) was used. Results showed no difference between the four powder lots. However, during the screening tests of powder lot Th-D-17, a green pellet end-defect occurred during pressing. The defect normally appeared on the top end of the pellet as a shallow surface flake, scale, or blister. The defect occurred regardless of pressure and was not the typical end-cap type defect usually associated with higher pressures. The problem, which continued on subsequent powder lots, could not be directly correlated to any of the wide range of ORNL denitration conditions.

The green pellet end-defect occurred during ejection from the die. It was prevented by restraining the pellet during ejection. A feature on the automatic hydraulic pellet press allows the top punch to retain a slight pressure on the pellet while it is being ejected. This compression on the pellet during ejection prevents the end-defect and also allows high pressures to be used during pellet pressing.

To confirm that some new, unknown variable was not causing the pellet end-defect, screening tests were repeated on the Th-D-5 powder lot. The hydraulic top-punch hold-down feature was not necessary to press acceptable green pellets. This powder lot was considered typical of the earlier lots. In addition, acceptable pellets could be pressed using the top-punch hold-down with the Th-D-5 powder. To maintain integrity in the test pellets, the hold-down on ejection was used on the balance of the powder lots evaluated. However, efforts were continued to determine the reason for the pressing defect.

End-defects appear to be related to powder morphology. Comparisons were made between the Th-D-5 powder, which produced acceptable green pellets,

pellets, and Th-D-17 powder, which required the top-punch hold-down feature during pellet ejection. These comparisons included:

- thermal gravimetric analysis of calcination/reduction cycle
- scanning electron microscopy (SEM) of particle shape
- particle size distribution of calcined powders

A thermal gravimetric analysis (TGA) that compares the calcination/reduction cycle of Th-D-5 and Th-D-17 powders is shown in Figure 10. Weight loss started at about 100°C for the Th-D-5 powder, whereas weight loss for the Th-D-17 powder did not start until about 500°C. Weight loss differences probably were due to the higher denitration furnace temperature of 525°C for Th-D-17 powder compared with 430°C for the Th-D-5 powder. Greater weight loss (Table 4) was observed on lots Th-D-4 through -7 that produced defect-free green pellets. However, when a comparison was made of the other powder lots (Table 1), the denitration temperature included a wide range. The ORNL denitration conditions and the pellet end-defect could not be directly correlated.

Scanning electron microscopy was used to examine the particle morphology of powder lots Th-D-5 and -17 at magnifications up to 10,000 (Figures 11 and 12). Both powders had a very fine particle size with a tendency for small agglomerates. The small particle size was also confirmed by the high surface area of these powders (Table 4). The Th-D-5 powder agglomerates are made of more uniform particles than are agglomerates of the Th-D-17 sample. Agglomerates of the Th-D-17 powder lacked uniformity. This lack of particle uniformity created inter-agglomerate voids, which make this powder more difficult to pack, and may explain the lower tap density on the Th-D-17 powder.

Other powder lots did not contain the uniform agglomerates observed in the Th-D-5 powder; however, the extreme lack of uniformity of the Th-D-17 powder was not evident in any of the additional powder lots examined. The SEM examination could not be considered conclusive, although the pellet end-defect apparently relates to particle and agglomerate size, shape and distribution. The distribution of particle size, shape, and density shown in the SEM micrographs could affect the packing of the powder.

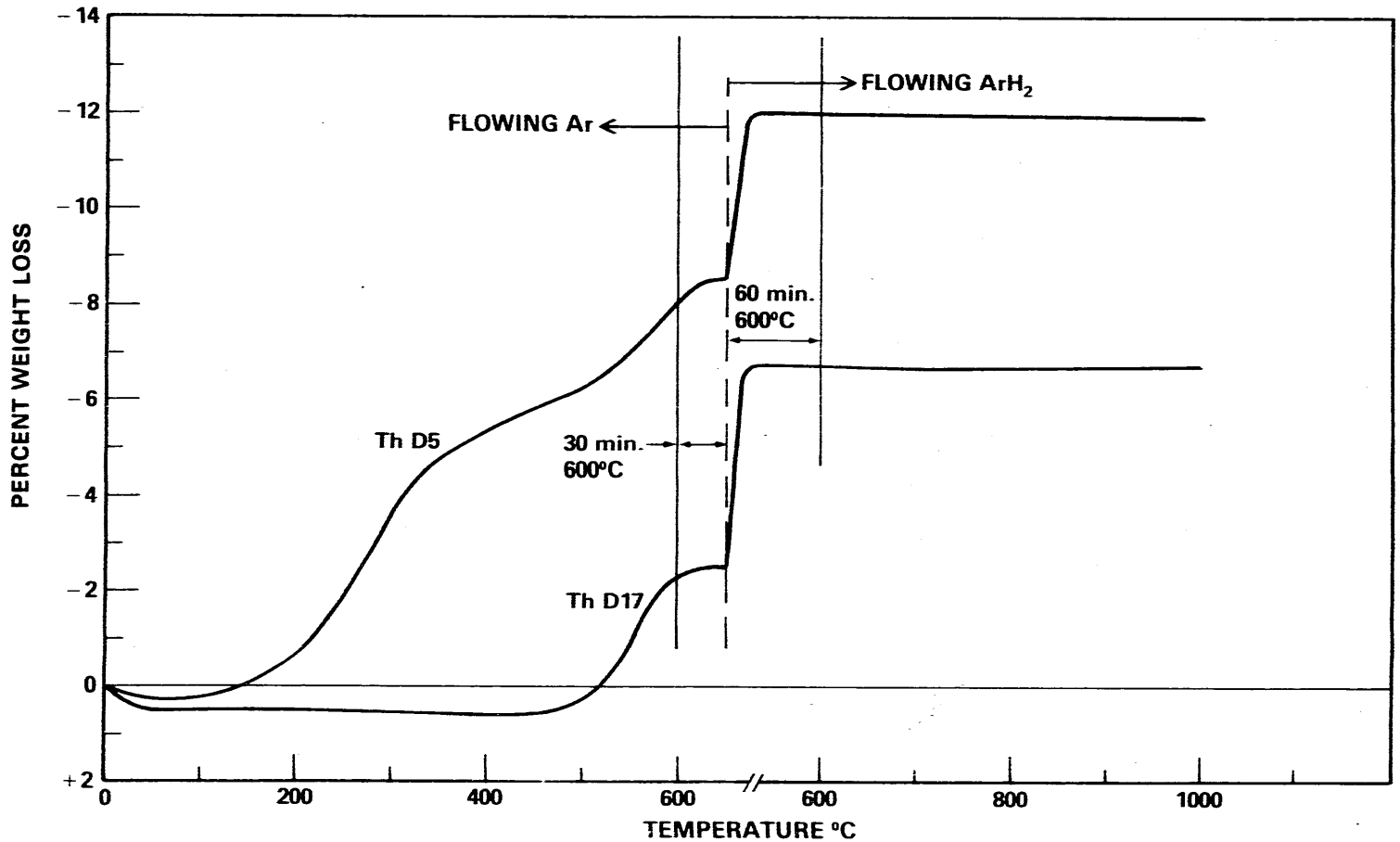


FIGURE 10. Weight Loss as a Function of Temperature for Powder Lot Th-D-5 and Th-D-17.

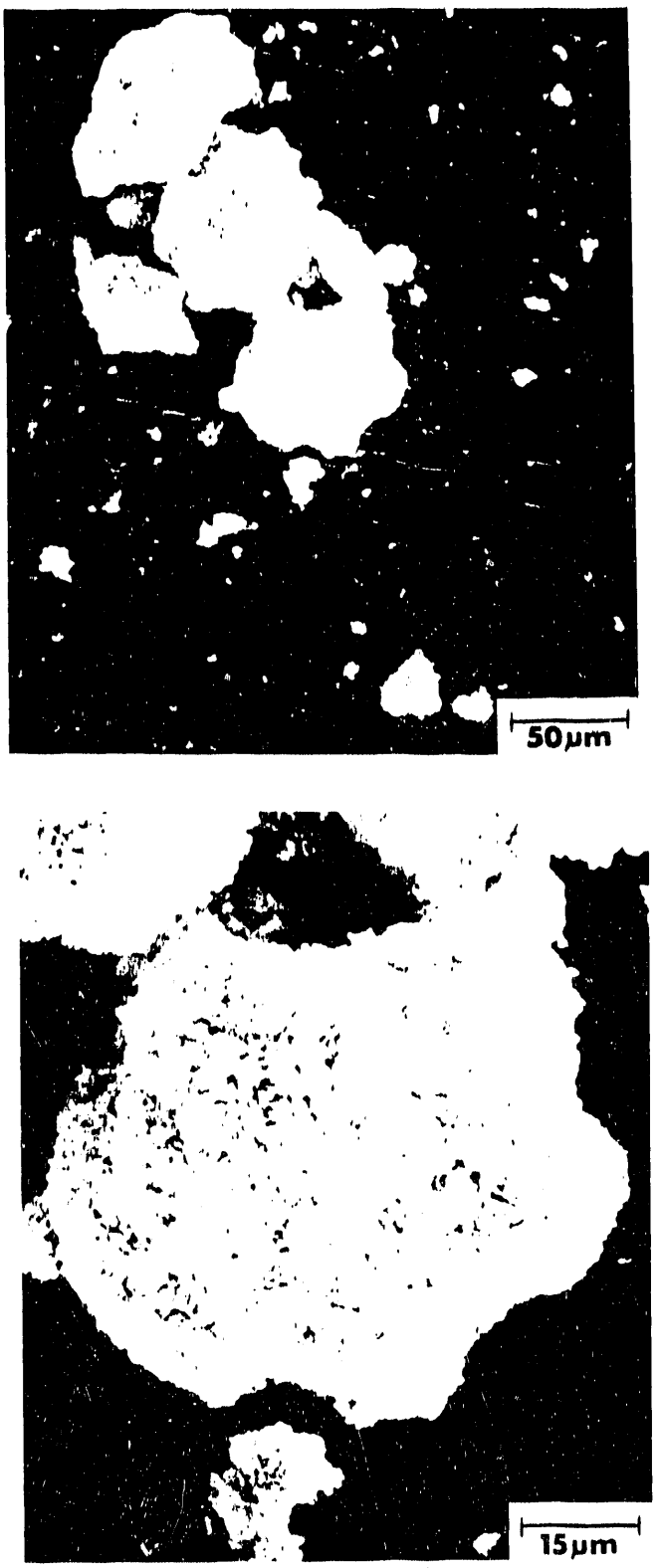


FIGURE 11. Scanning Electron Micrographs (SEM) of Powder Lot Th-D-5 After Calcination and Reduction (Screening Test 600°C, 4 h, 50% H_2-Ar).

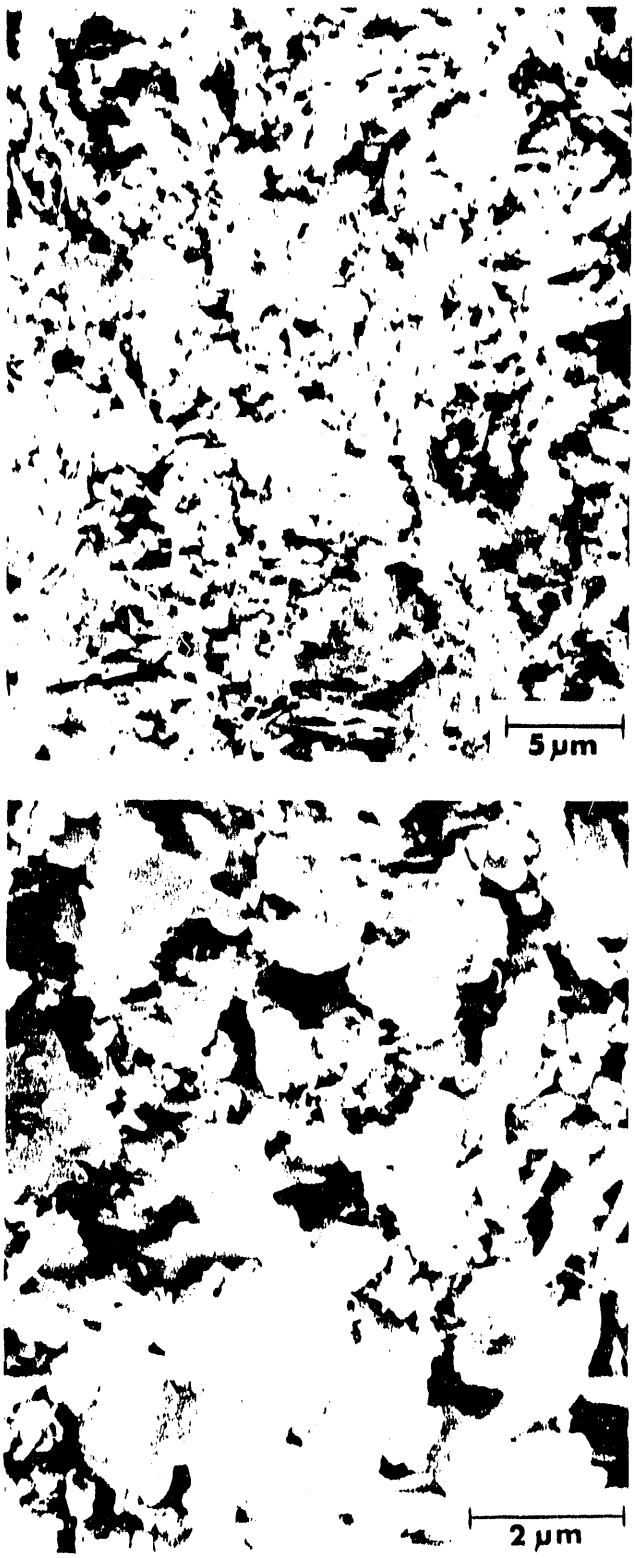


FIGURE 11. (Continued)

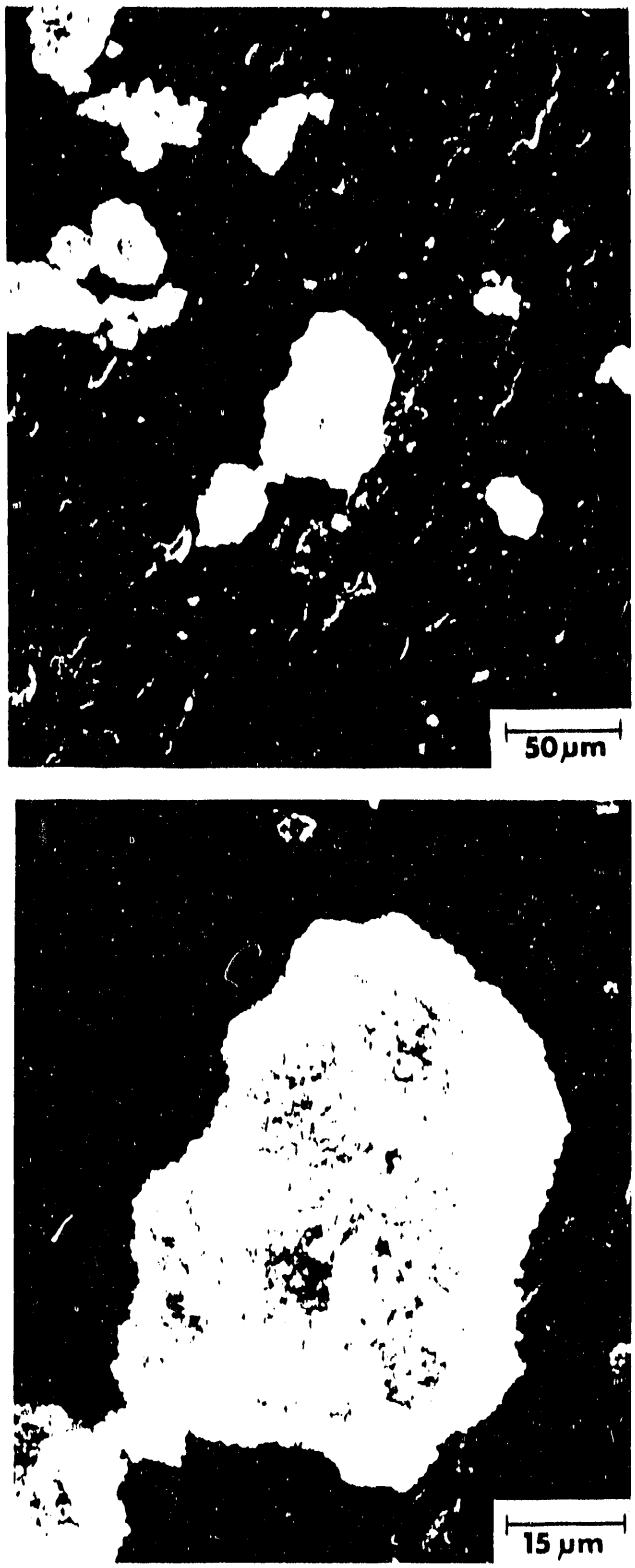


FIGURE 12. Scanning Electron Micrographs (SEM) of Powder Lot Th-D-17 After Calcination and Reduction (Screening Test 600°C, 4 h, 50% H_2-Ar).

FIGURE 12. (Continued)

Particle size distribution of powder lots Th-D-5 and Th-D-17 was determined by a centrifuge-sedimentation method. This method is normally used for quantitative analysis to evaluate particle distribution for powder compaction or for use with surface-area measurements to determine powder sinterability.

When the particle size distribution comparisons on the thermally denitrated powder lots were made, the Th-D-5 powder, which pressed satisfactorily, included 24% of the particles in the submicron range. The powder lots that produced end-defects contained a larger quantity of submicron fines. The Th-D-17 powder sample had 33% submicron fines and powder lots Th-D-22 through -25 contained an average of 45% in the submicron range. The excessive powder fines could be causing the pressing defect; however, as with the SEM examination, this observation could not be considered conclusive.

To determine whether pressing defects associated with the powder produced by the continuous rotary kiln could be eliminated by reducing the excessive powder fines, a batch denitration run was made by ORNL under conditions to reduce the fines concentration. This procedure entailed a slow-rate (about 20 h at 210°C) batch operation instead of the continuous rotary method. The UO_3 crystals were allowed to grow, which resulted in a mean particle size of 4 μm. In contrast to the rotary kiln powder lots, only about 10% of this batch denitration (Th-D-26) was submicron. This powder produced high density green pellets without any pellet end-defects and did not require the top-punch hold-down.

Th-D-26 powder sintered to a maximum of 90 to 92% TD when pressed to the optimum green density. The uniform, low density pellet structure (Figure 13) was defect-free. This powder lot had a surface area of 3.26 m^2/g and a tap density of 1.68 g/cm^3. These relatively large, dense particles are related to the slow-rate batch denitration procedure. Additional development of this procedure could be beneficial to producing a powder that can be processed directly, using conventional steps, to the specified Fast Breeder Reactor (FBR) densities of 90% TD.

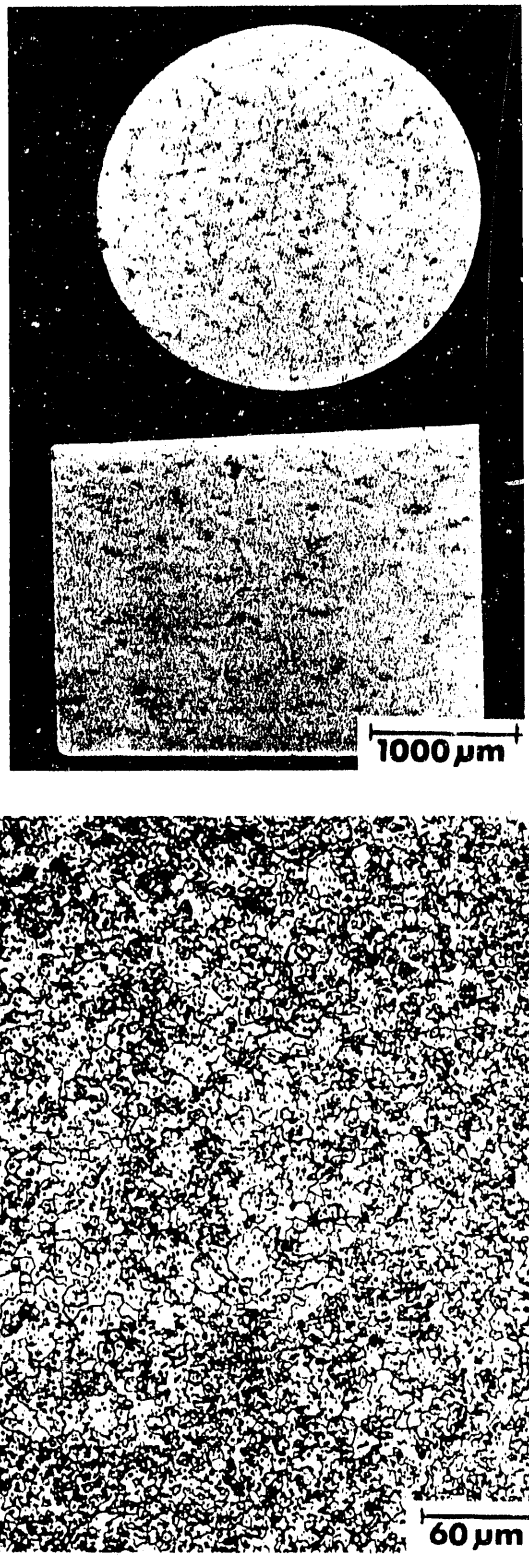


FIGURE 13. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-26, 89.5% TD.

FBR DENSITIES

In addition to the FBR densities achieved with the special Th-D-26 powder lot, developmental studies were made using the following techniques to obtain the desired low density:

- increasing calcination temperatures to reduce sinterability
- adding volatile poreformers to produce pores
- using precursor, UO_3 poreformer additions.

CALCINATION/REDUCTION STUDIES

Increased calcination and reduction temperatures were investigated as a method to further characterize the thermally denitrated powder and to reduce and control the sinterability of this highly active powder. Specific surface area is usually regarded as a good indicator of powder sinterability. Heat treatment of UO_2 is a well-known method to decrease the surface area and deactivate the sinterability of a powder[3,4]. This may be accomplished by a thermal treatment of the UO_2 during powder preparation, or it may be controlled by temperature during the conversion and reduction of the UO_2 precursor[5,6,7].

The wide range of thermally denitrated tube temperatures (Table 1) had little, if any, effect on the surface area or sinterability when NH_4NO_3 was included in the feed solution. Likewise, in the following calcination/reduction temperature tests increasing the calcining temperature to 1000°C had limited effect on sintered density, but had major impact on pellet quality and powder properties.

Powder lots Th-D-17 and -22 were chosen for the increased calcination/reduction temperature tests. These two powder lots were prepared at different temperatures, product rates, and feed concentrations (see Table 1); however, they were both processed with ammonium nitrate in the feed solution. After calcination and reduction at 600°C in the screening tests, the UO_2 powder properties were similar (Table 4). In both cases test pellets sintered to 97% TD.

The series of increased temperatures included six calcination/reduction runs ranging from 600 to 1000°C. All runs were for 4 h at temperature. The typical screening test process used included heating in argon, reducing in 50% hydrogen/50% argon, and cooling in argon. Test data, process conditions, and inspection results are shown in Table 7 for the Th-D-17 powder lot and in Table 8 for the Th-D-22 powder lot. The powder surface area decreased as expected (Figure 14) from >10 m^2/g at 600°C to <1 m^2/g at 1000°C. Likewise, the O/M ratio dropped (Figure 15) with increased temperature. However, the sintered density decreased only slightly with the increased calcination temperature. Calcination/reduction up to 800°C yielded high quality test pellets that sintered to 97% TD. Powder calcined above 800°C yielded pellets with poor green and sintered strength, but the pellets still sintered to densities of 95% TD. These results indicate that FBR density would be difficult to control by increasing calcination temperature. Very little difference was seen in comparing the properties and fabrication of the two powder lots.

POREFORMERS

The control of UO_2 fuel pellet densities by incorporating volatile additives (poreformers) has been widely reported[5,6,8]. Poreformers are of particular interest in the manufacture of irradiation-stable fuel when an extremely active powder is used. By appropriate selection of size, the addition of the poreformer can create large stable pores in a dense 97 to 99% TD matrix and minimize the amount of extremely fine, unstable porosity. Several different poreformers were evaluated at PNL in a study of fuel densification[6]. This technique was useful for obtaining densities as low as 85% TD in a low density, PuO_2-UO_2 fabrication study[5]. An extensive experimental program was conducted by Westinghouse Research Laboratories[8] to determine the most suitable poreformer for the control of sintered density. Various additives, including uranyl and ammonium salts, were included in this study.

Several different additives were used in this study with highly active thermal denitrated powder. These included: Polyethylene glycol, polyvinyl

TABLE 7. Effect of Temperature on Powder Properties and Fabrication Characteristics of Powder Lot Th-D-17.

	Temperature, °C					
	600	700	800	850	900	1000
Weight Loss (%)	7.1	7.5	7.7	7.6	8.4	7.8
O/M	2.18	2.16	2.08	2.06	2.05	NA
Tap Density (g/cm^3)	0.97	1.04	1.07	1.11	1.07	1.44
Surface Area (m^2/g)	10.61	7.46	4.4	3.08	2.99	0.84
Green Density (g/cm^3)	5.17	4.92	5.42	5.60	5.98	NA
Immersion Density (% TD)	97.65	97.08	97.36	96.40	95.38	94.45

Note: Pellet quality was acceptable except at 900 and 1000°C.

TABLE 8. Effect of Temperature on Powder Properties and Fabrication Characteristics of Powder Lot Th-D-22.

	Temperature, °C					
	600	700	800	850	900	1000
Weight Loss (%)	11.2	11.6	11.7	11.5	12.0	12.4
O/M	2.16	2.12	2.08	2.05	2.04	NA
Tap Density (g/cm^3)	0.87	0.94	1.01	1.04	0.95	1.19
Surface Area (m^2/g)	10.33	6.70	4.4	3.34	2.94	0.84
Green Density (g/cm^3)	5.06	4.96	5.40	5.44	5.52	6.11
Immersion Density (% TD)	97.70	96.67	97.13	96.85	95.38	95.80

Note: Pellet quality was acceptable except at 900 and 1000°C.

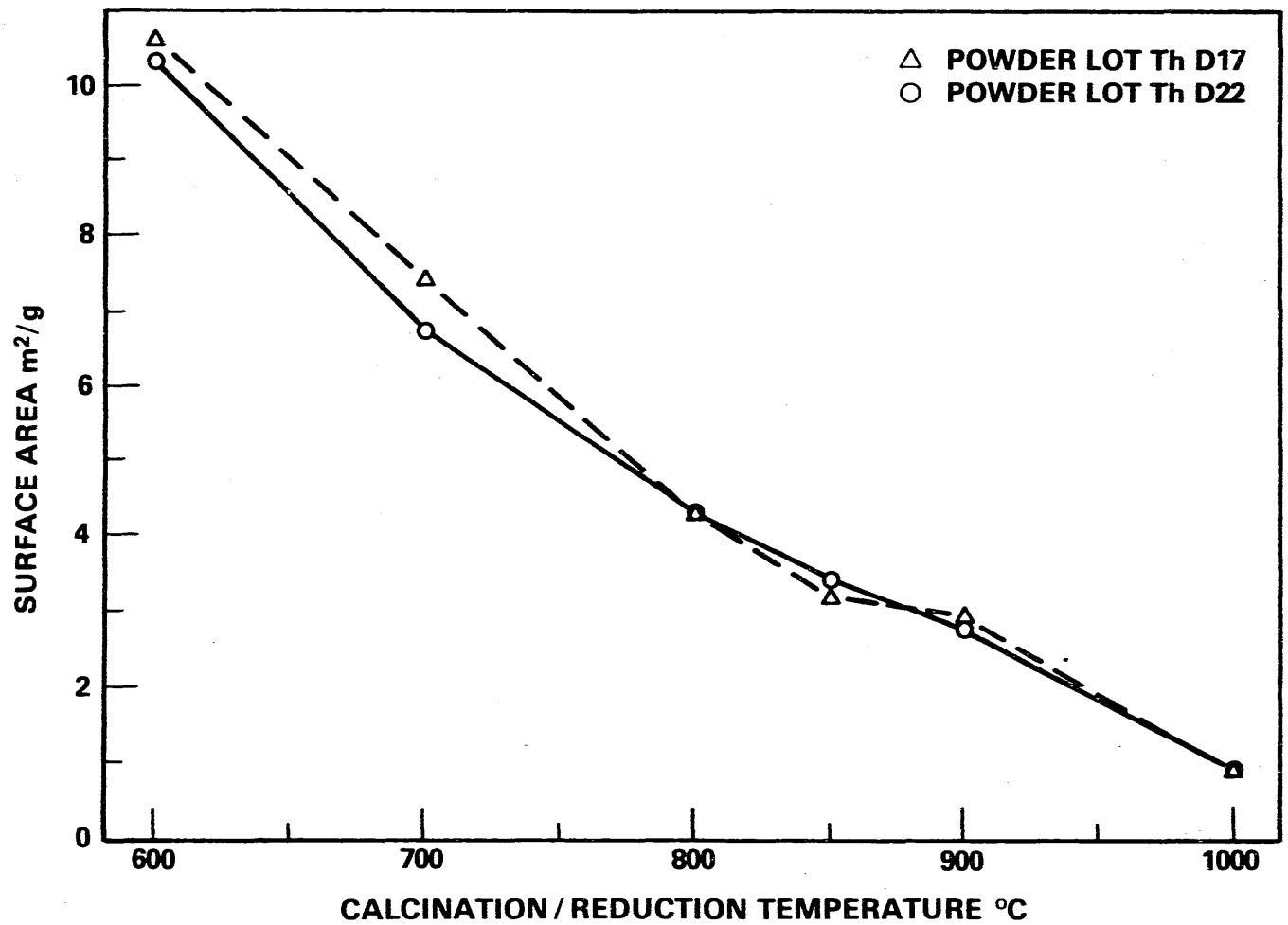


FIGURE 14. The Effect of the Calcination/Reduction Temperature on the Surface Area of Thermally Denitrated UO_2 Powder.

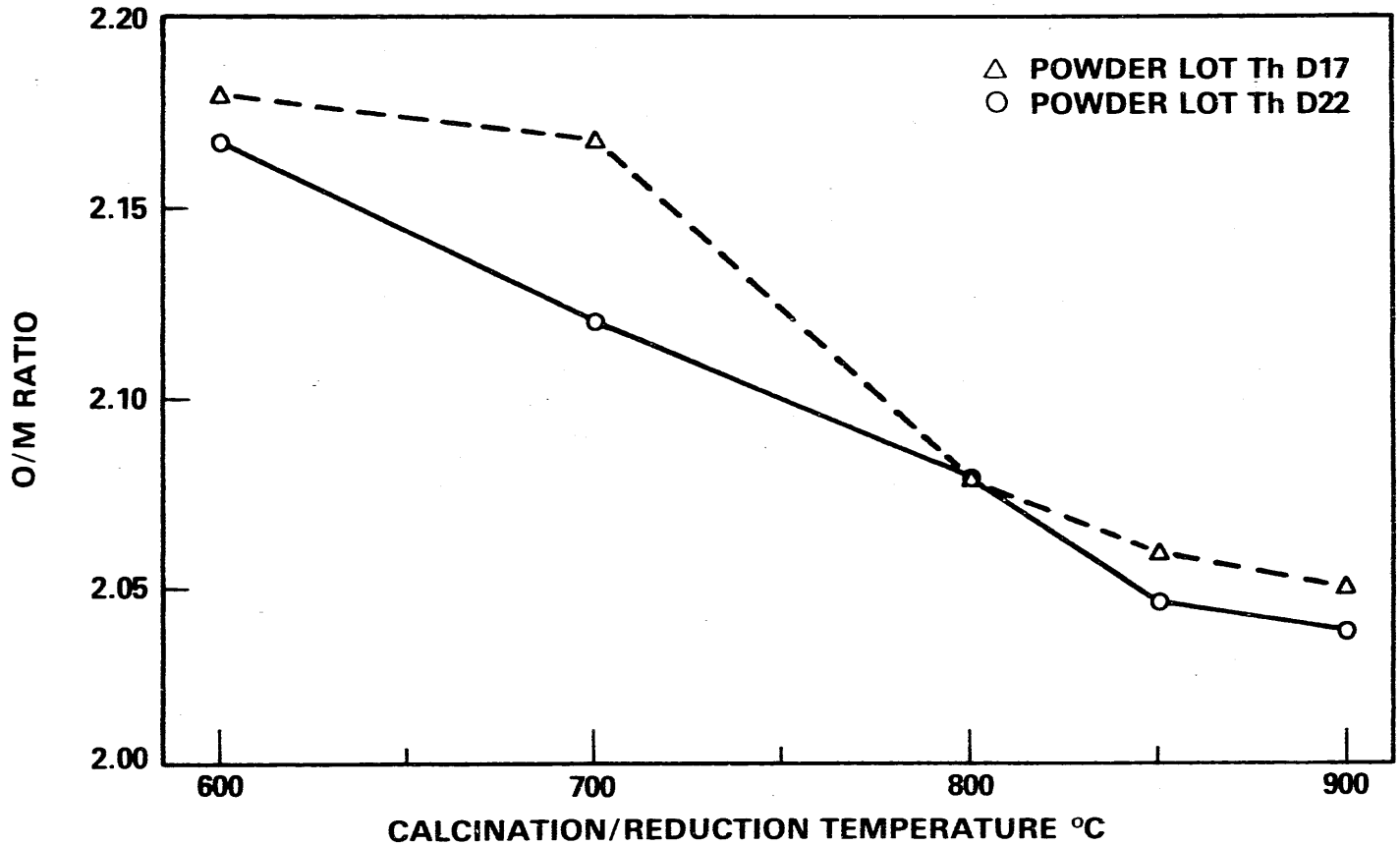


FIGURE 15. The Effect of the Calcination/Reduction Temperature on the Oxygen/Uranium Ratio of Thermally Denitrated UO_2 Powder.

alcohol and various ammonium salts. All of these poreformers effectively reduced pellet density; however, in the present study added emphasis was placed on ammonium oxalate (AO) which was easy to process and produced somewhat spherical shaped pores with smooth and rounded surfaces. As reported by the Westinghouse study, "the AO additive produced the 'cleanest' looking pore structure of all the additives"(8).

The AO particle size fraction and shape (Figure 16) determines the pore size and shape in the pellet. The homogenous distribution or mixing of the poreformer is important to maintaining a uniform microstructure. After calcining and reducing the UO_3, the highly sinterable UO_2 powder is granulated to -100 mesh. The powder is then blended with the size fraction of AO to produce the desired density and microstructure. After blending the poreformer, the powder is slugged and granulated, and then the process flow is returned to normal. Adding the poreformer to the UO_2 before the slugging "locks-in" the pores in the UO_2 granules to provide a more uniform and homogeneous microstructure.

One of the earliest PNL tests used AO in a -140 +200 mesh size range (Figure 17) with powder lot Th-D-12 (from the NLO scale-up run). This microstructure is compared with a smaller size fraction -200 + 325 mesh AO poreformer (Figure 18) used in the mixture of powder lots Th-D-4 through -7. The size of the poreformer particle determines the size voids in the microstructure while the amount of poreformer controls density. An approximate 3% density reduction can be expected per 1 wt% of the AO poreformer. The linear relationship between the sintered density and percentage of AO poreformer (Figure 19) allows precise density control. The target FBR density (88 to 92% TD) was achieved in a mixture of lots Th-D-4 through -7 with 2 wt% AO (Figure 18) and with 2.5 wt% AO (Figure 20).

Pellets within the FBR density range were also made using powder lot Th-D-18 with 2 wt% AO. Figure 21 shows the reference standard for Th-D-18 without the poreformer. Figures 22 and 23 show the transverse and longitudinal sections with no evidence of pore distortion due to pressing direction.

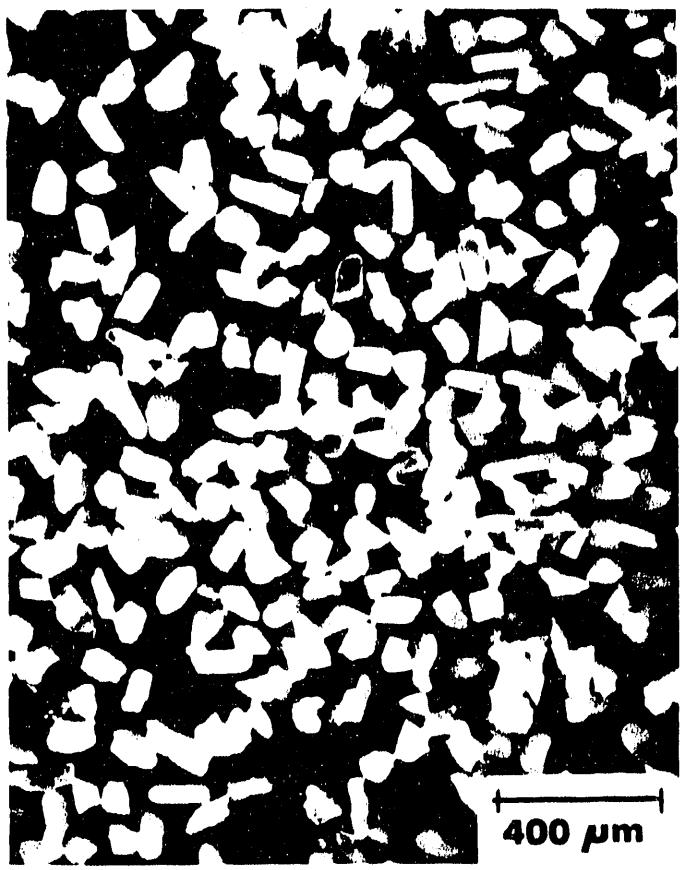


FIGURE 16. Micrograph of Ammonium Oxalate Particles (-200 +230 Mesh) Used as Poreformers in UO_2 Pellets.

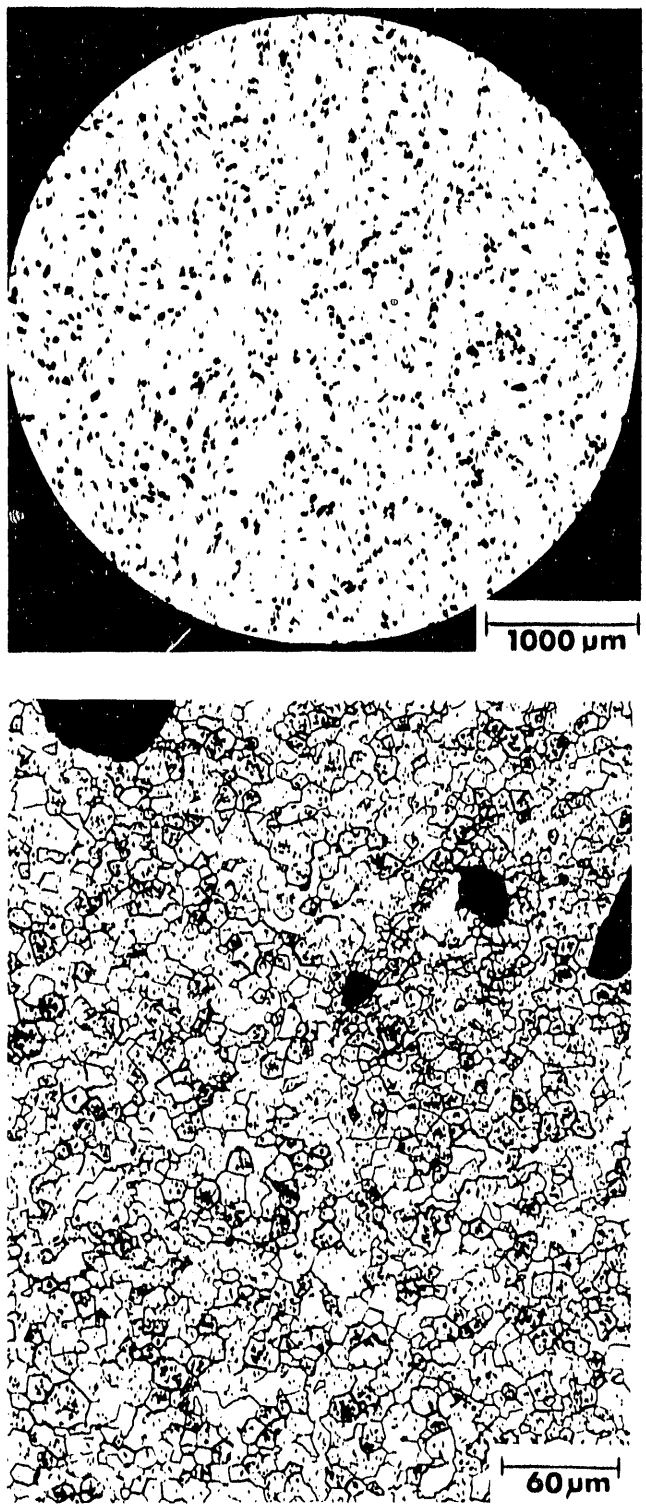
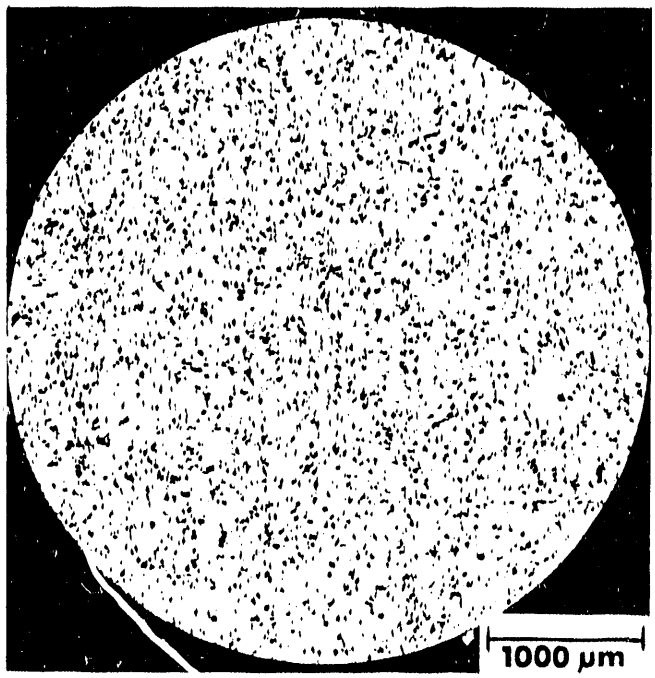


FIGURE 17. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-12, Using 1.75 wt% AO -140 +200 Mesh as Pore-former, 91.1% TD.



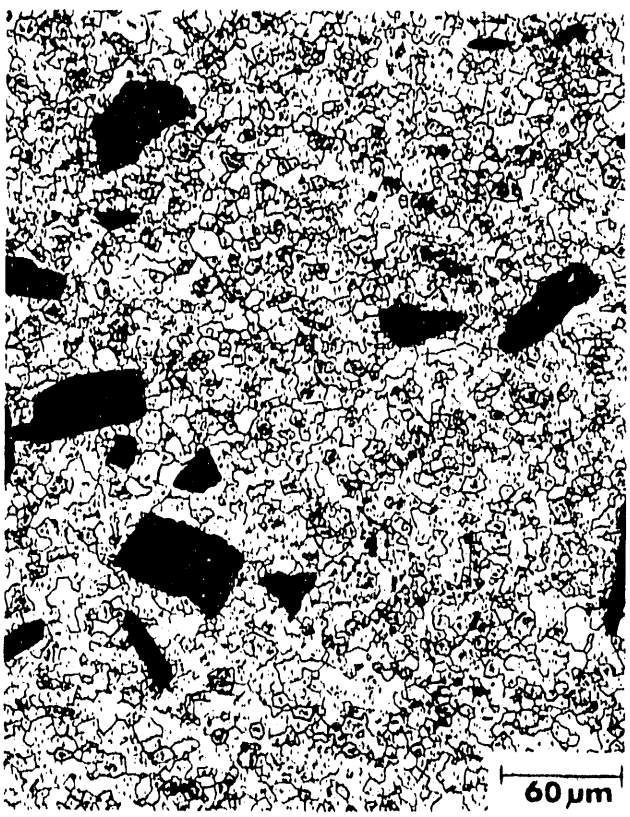


FIGURE 18. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-4 through -7 (Composite), Using 2 wt% AO -200 +325 Mesh as Poreformer, 91.4% TD.

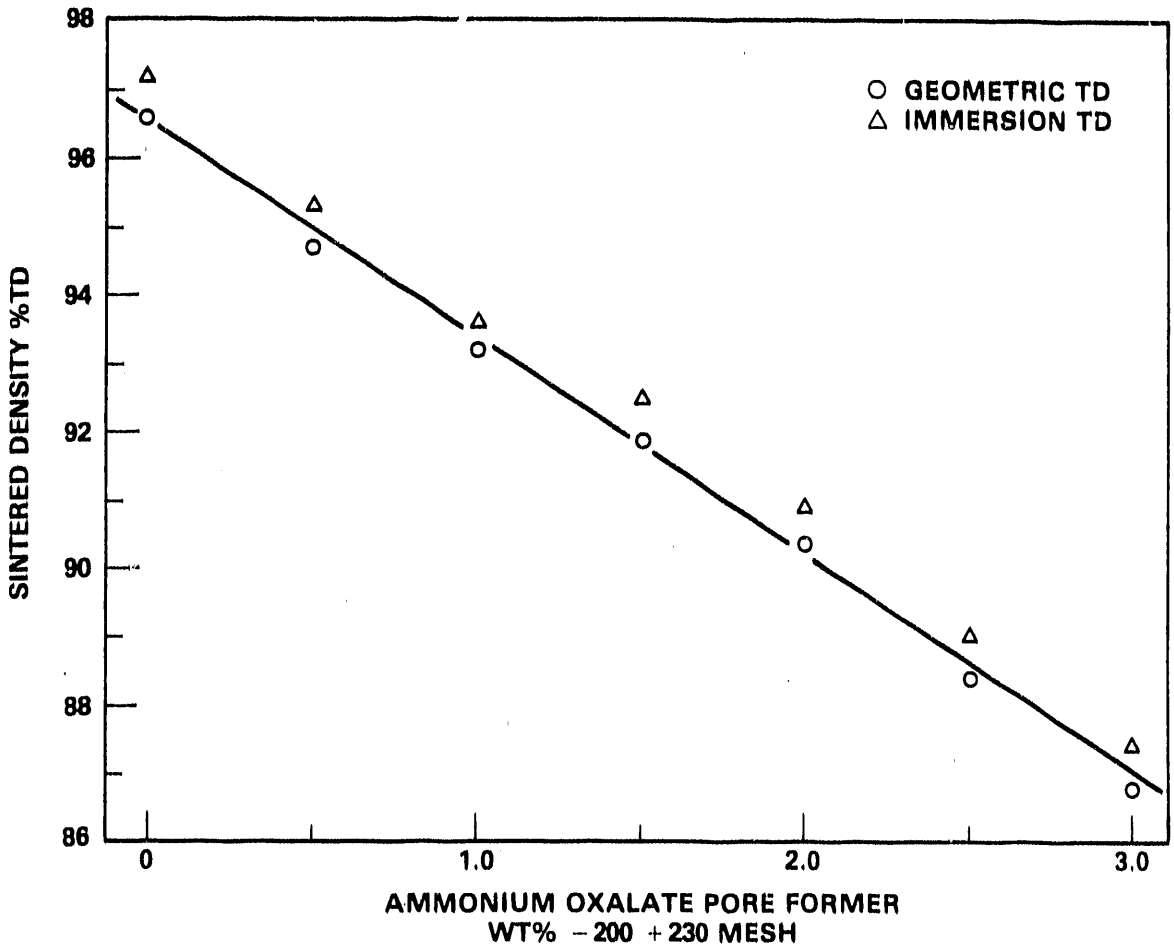


FIGURE 19. The Effect of Ammonium Oxalate Poreformer on Sintered Density of UO_2 Pellets.

Carbon content of sintered pellets fabricated with the AO poreformer was 158 ppm when the pellets were sintered with the routine heating rate of 150°C/h to 450°C and 300°C/h to 1700°C. The level was slightly above the limit of 150 ppm.[a] It was reduced to 34 ppm in subsequent tests, when the heating rate was changed to 50°C/h between 300 and 400°C. This change was made after a TGA run (Figure 24) showed the AO was volatilized above 300°C.

PRECURSOR GRANULES AS POREFORMERS

This technique utilizes a quantity of the UO_3 fuel precursor granules blended with the highly sinterable thermal denitrated UO_2. The desired porosity is obtained during the sintering cycle by the decomposition, reduction, and localized shrinkage of the UO_3 granules.

The attractive features of this method include reduced probability of impurities due to additives, and uniform powder mixing due to minimal density differences between the UO_2 powder and the UO_3 granule.

For this study, development work on this technique was limited. Additions of 10, 15 and 20 wt% of the UO_3 granules were blended with the UO_2 (a composite of lots Th-D-23 through -25). The procedure includes slugging, granulating, and sizing the UO_3 granule and blending these dense, hard granules with the granulated UO_2 in the lubricant blending operation. When the 20 wt% -170 +200 mesh hard granules of UO_3 were blended with granulated UO_2 and processed, the pellet density was 92.5% TD, producing a porous and non-uniform microstructure (Figure 25). This technique could be of interest in producing pellets at FBR densities, but requires further development.

If the UO_3 is blended with the base UO_2 in the fine, as-received form, before preslugging, it has minimal effect on reducing density. A 20 wt% addition of the fine as-received UO_3 produced sintered pellets about 95% TD.

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[a] From RDT-13-6.

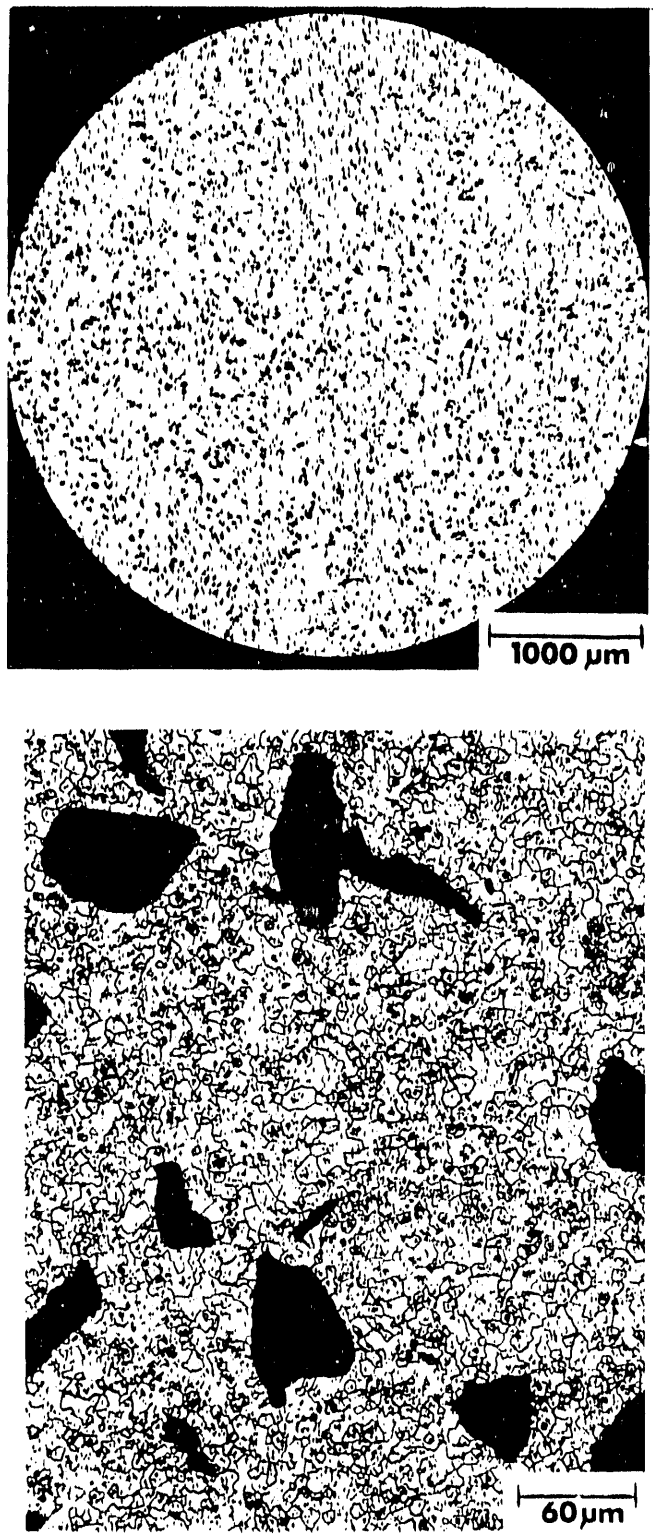


FIGURE 20. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-4 through -7 (Composite), Using a 2.5 wt% AO (-200 +325 Mesh Particles) as Poreformer, 90.0% TD.

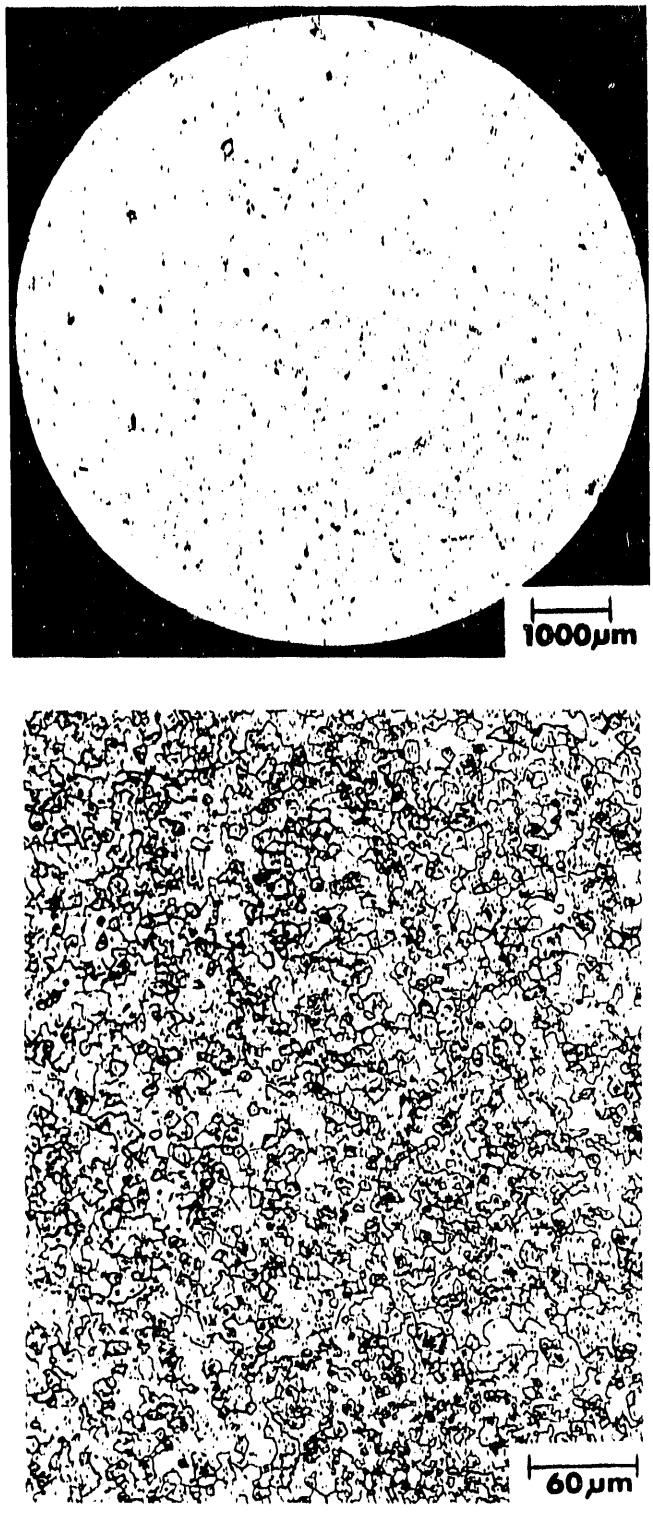


FIGURE 21. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-18; Reference Standard Pellet Without Poreformer, 97.3% TD.

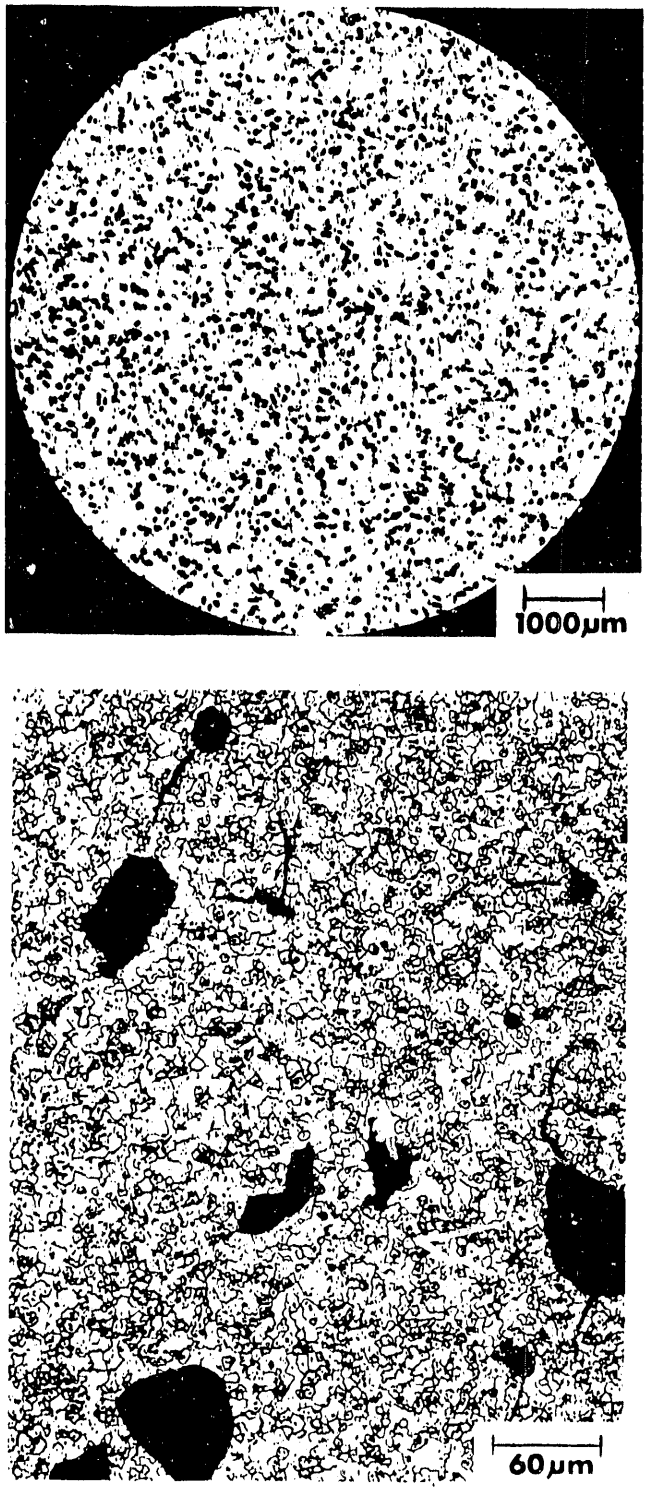
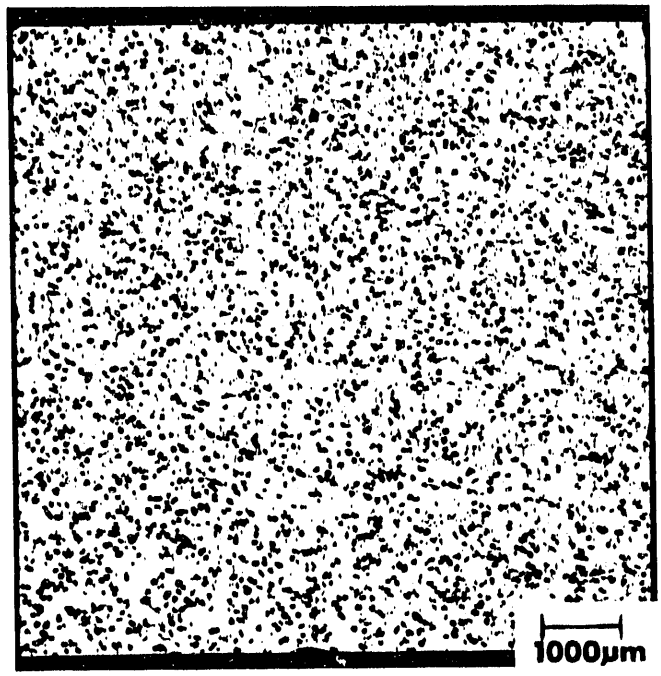


FIGURE 22. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-18, Using 2 wt% AO (-200 +325 Mesh Particles) as Poreformer, 89.8% TD (Transverse).



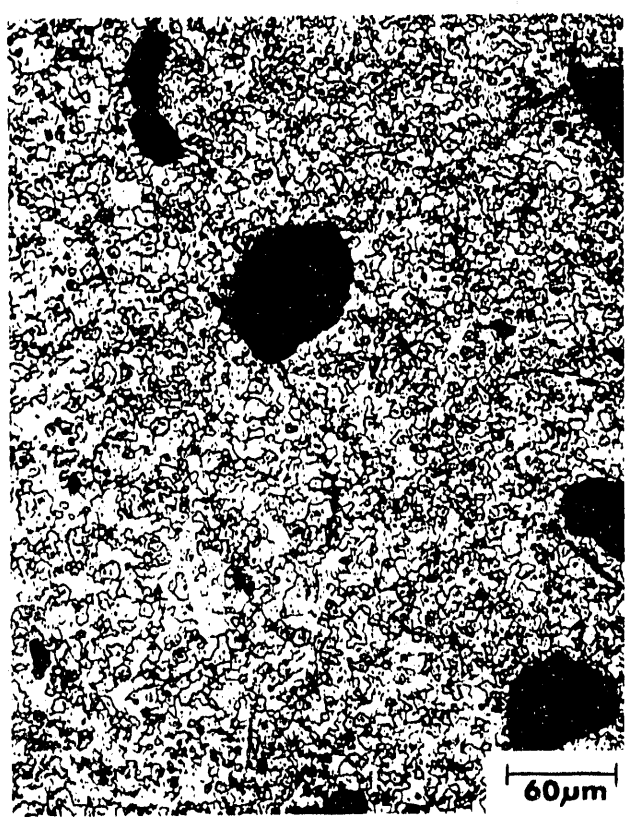


FIGURE 23. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-18, Using 2 wt% AO (-200 +325 Mesh Particles) as Poreformer, 89.8% TD (Longitudinal).

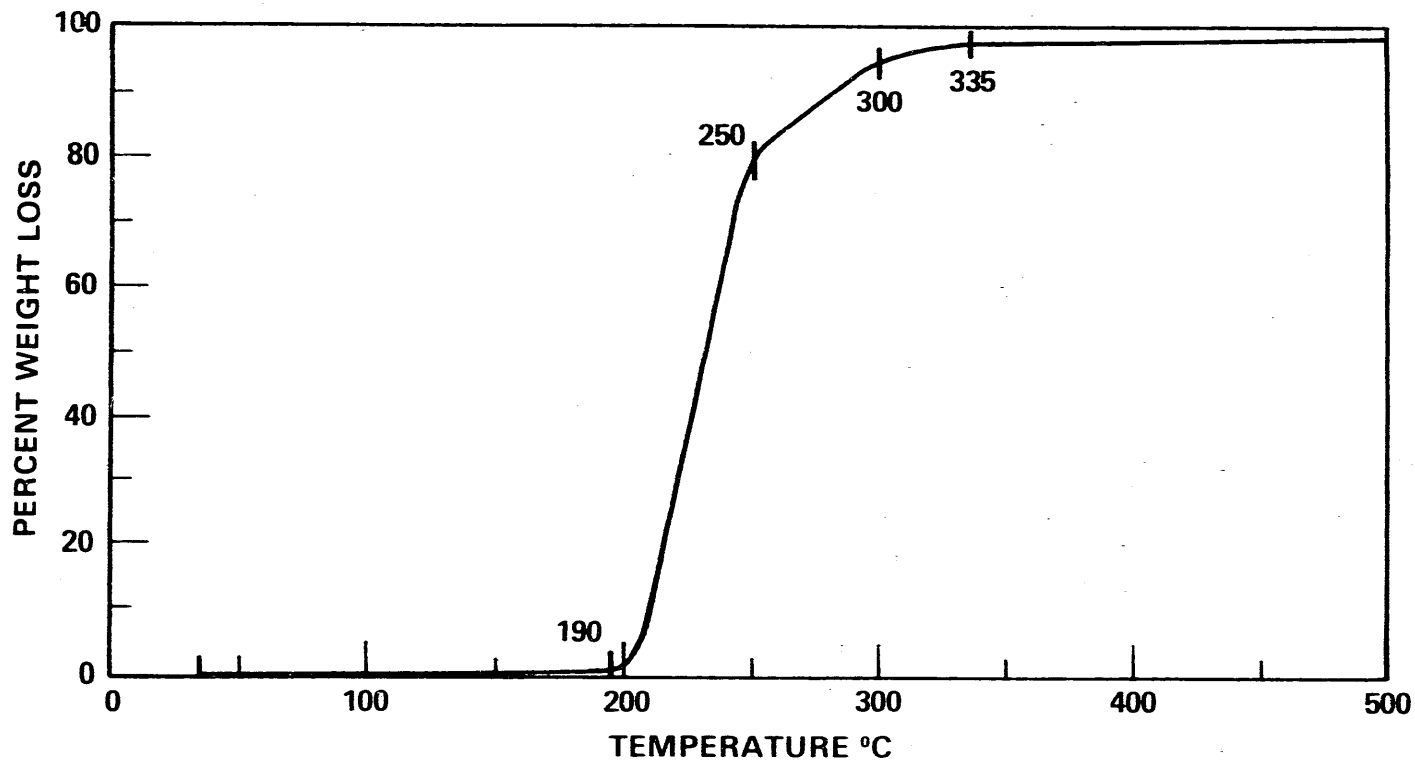


FIGURE 24. Weight Loss of Ammonium Oxalate (-140 +200 Mesh Particles) as a Function of Temperature, Rate 2°/m.

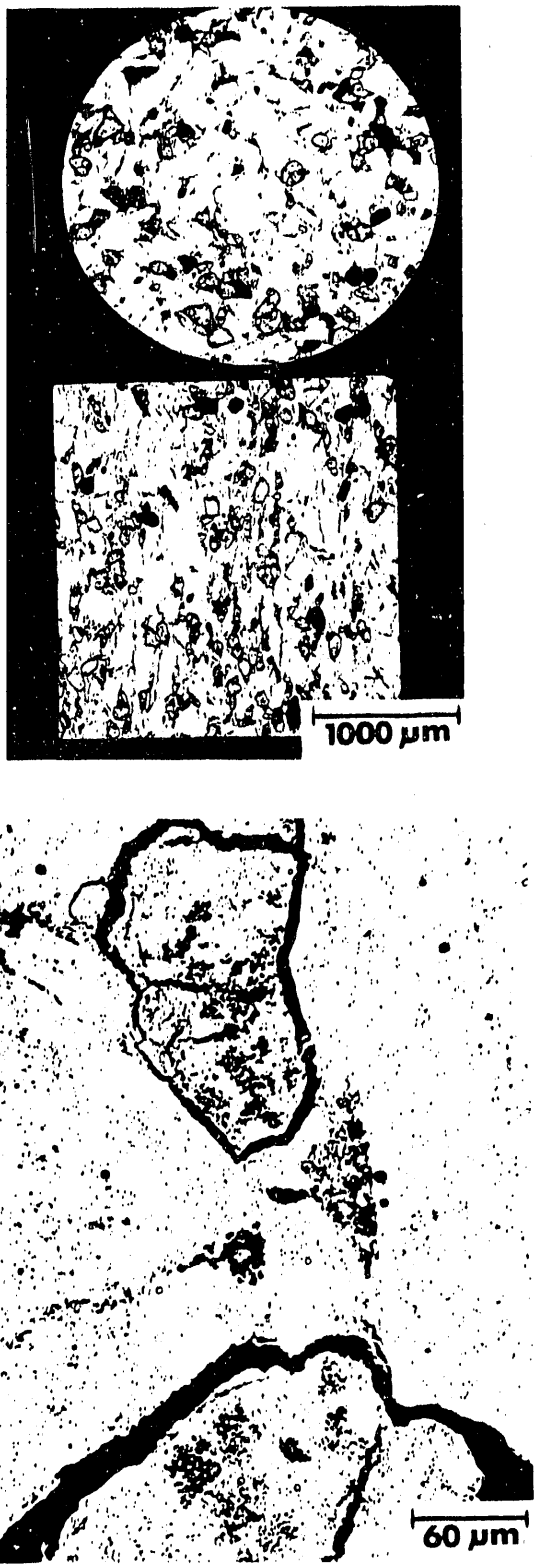


FIGURE 25. Microstructure of UO_2 Pellet Made from Powder Lot Th-D-23 through -25 (Composite), Using 20 wt% UO_3 as a Precursor Poreformer, 92.5% TD.

IMPURITY ANALYSIS

Impurity analyses were made for two of the thermal denitration powder lots (Table 9) after calcination and reduction. Apparently, the only significant impurity was the high level of nitrogen (1000 ppm) in the powder after the 4 h, 600°C calcine treatment. Up to 18 h additional time at 600°C had little effect and only reduced this level to 950 ppm. However, higher calcination/reduction temperatures showed a continued reduction to 350 ppm at 900°C, 4 h. The nitrogen in sintered pellet was reported in three samples from 10 ppm to 50 ppm, well below the 200 ppm limit.[a]

[a]RDT-13-6 Standard.

TABLE 9. Impurity Analyses of Thermal Denitrated UO_2 Powder Lots Th-D-17 and Th-D-12.

Element	RDT-13-2 Limits in ppm by wt UO_2 Powder	UO_2 Powder Analysis Th-D-17	Th-D-12
Aluminum	500	<50	<50
Beryllium	20	<2	<2
Boron	10	0.03	0.01
Cadmium	20	<2	<2
Calcium	100	60	30
Carbon	150	-	-
Chlorine	25	<10	<10
Chromium	200	<25	<40
Cobalt	10	1	0.1
Fluorine	25	ND	ND
Iron	400	300	400
Lithium	10	<1	<1
Magnesium	25	<10	<10
Nickel	400	50	50
Nitride Nitrogen	200	1000	1100(1)
Phosphorus	50	10	100
Potassium	200	<20	<20
Sodium	500	<100	<100
Sulfur	300	ND	ND
Vanadium	400	0.5	0.2
Tantalum	400	0.5	0.5
Tungsten	100	0.15	0.15
The sum of copper, zinc, silicon, and titanium	800	260	290
The sum of silver, manganese, molybdenum, lead and tin	200	50	70
The sum of samarium, europium, gadolinium, and dysprosium	100	<0.65	<0.65

(1)Nitrogen ranges from 700 to 1100 ppm in UO_2, calcined and reduced 600°C -4 h; however the nitrogen content was reduced to between 10 and 50 ppm after sintering.

RESINTER TEST

A random selection of thermally denitrated test pellets, including the high densities of ∿97% TD and the low FBR densities of ∿90% TD were subjected to a 24 h, 1700°C resinter test. The initial sintering cycle for these pellets was 1700°C for 8 h. After resintering, the density of the two groups of pellets increased an average of 0.6% TD with the change ranging from 0.1 to 1.1% TD. As a point of interest, the density after an initial sintering cycle of 4 h at 1700°C was ∿0.5% TD lower than when the test pellets were sintered for 8 h.

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